POWER AND THERMAL TECHNOLOGIES FOR AIR AND SPACE -- SCIENTIFIC RESEARCH PROGRAM

Delivery Order 0016: Developing and Processing High Energy Density Polymer Film Dielectrics for High Temperature Air Force Power Electronic Applications

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Final Report

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14. ABSTRACT
The objective of the delivery order (DO) is to develop high energy density polymer dielectrics and optimize their film processing methods for utilization in stacked or rolled capacitor architectures. An emphasis should be placed upon obtaining a material with a high energy density (> 10 J/cc), a low dissipation factor (0.001 percent) and a rapid discharge rate (µs to ns), all of which are stable over a wide temperature range (-55 ℃ to 250 ℃), and up to high frequencies (>400 kHz when packaged). A dielectric film with a graceful failure mechanism is also desirable, but without sacrificing the rapid discharge rate (electrode conductivity).

-- See back for alternate abstract --

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14. ABSTRACT, concluded

Requirements for wide-temperature Air Force Power Electronics applications have been addressed via the in-house design, development and dielectric investigations of several high temperature polymer films. Towards meeting the objective of electro-mechanical stability and reliability for high temperature ($\geq$ 300 ºC) power conditioning capacitor applications, the dielectric properties of thermally robust polymer thin films with high glass transition temperatures (T_gs, 305-450 ºC) as well as high thermal stabilities (470-520 ºC) were evaluated. The overall focus of the study was on wide-temperature measurements of film capacitance, dissipation factor as well as insulation resistance and the effects of thermal cycling on polymer dielectric stability. After initial screening of a broad spectrum of polymeric materials, the dielectric investigations specifically focused on the extensive wide-temperature evaluation of metalized thin films of a fluorinated polybenzoxazole copolymer with a hydroxyl pendant (6F-Co-PBO, T_g =375 ºC) and a fluorenyl polyester incorporating a diamond-like hydrocarbon unit (FDAPE, T_g = 450 ºC) in the RT-350 ºC range; a comparative evaluation of the state-of-the-art, commercial fluorenyl polyester film FPE, with a glass transition temperature of 330 ºC, was also performed. While the thermal cycling studies indicated that the temperature coefficient of capacitance ranged from 2-3.5 % in the RT-350 ºC range for all the three films, FDAPE showed the lowest temperature-dependent DF and the highest insulation resistance among the three films examined. Average room temperature breakdown strengths for 6F-Co-PBO and FDAPE films ranged from 240 to 245 V/µm while it was measured to be 440V/µm for the FPE film under the same experimental conditions. However, optimization of the current solvent–based laboratory scale thin film fabrication process can potentially lead to higher film breakdown strengths for both FDAPE and 6F-Co-PBO films.

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FOREWORD

PREFACE

The objective of this program was to provide/examine high performance polymer films for potential utilization as thermally robust, high energy density dielectrics for Air Force Wide-Temperature Power Electronics Applications. The high temperature polymer film dielectric technology has been explored from the viewpoint of meeting the current stringent thermal requirements of operational reliability of AF power system conditioning capacitors up to or even exceeding 300ºC. Specifically, the high temperature film capacitor design would help support compact, robust electrical power systems and high temperature electric actuators as a part of the AF INVENT (Integrated Vehicle Energy Technology) Program.

1.0   Summary

Requirements for high temperature Air Force Power Electronics applications have been addressed via the in-house design, development and dielectric investigations of several high temperature polymer films. The design criteria were geared towards enhancing the performance reliability of the power systems at higher temperatures, thereby decreasing the thermal load for electronic system cooling. Towards meeting the objective of dielectric/electro-mechanical stability for wide-temperature power electronics applications, thermally robust thin polymer films with high glass transition temperatures (T_gs, 305-450ºC) as well as high thermal stabilities (470-520ºC) were evaluated for power conditioning capacitor applications for potential operation at $\geq$ 250ºC. It is expected that higher T_g polymer film dielectrics will enable fabrication of capacitors with higher reliability, and longer life upon cycling over the targeted range of temperatures (-55ºC to 250ºC). The overall focus of the study was on variable temperature measurements of film capacitance, dissipation factor (DF) as well as insulation resistance (IR) and the effects of thermal cycling on polymer dielectric stability. The relatively broad spectrum of polymeric materials comprised a fluorinated polyimide with an adamantyl ester pendant (PI-ADE), a fluorinated polybenzoxazole copolymer with a hydroxyl pendant (6F-Co-PBO) and a fluorenyl polyester incorporating a diamond-like hydrocarbon unit (FDAPE) in the backbone. Initial variable temperature studies (up to 250ºC and above) indicated a relatively low temperature coefficient of capacitance (TCC) (~ 2 %) for all the films, a characteristic desired for developing power conditioning capacitors for wide-temperature applications.

The second phase of the dielectric investigations specifically focused on the extensive wide-temperature evaluation of metalized thin films of 6F-Co-PBO (T_g =375ºC) and FDAPE (T_g = 450ºC) in the room temperature (RT)-350ºC range; a comparative evaluation of the state-of-the-art fluorenyl polyester film FPE, with a glass transition temperature of 330ºC, was also performed. The temperature coefficient of capacitance ranged from 2-3.5 % in the RT-350ºC range for the three films, FPE, FDAPE and 6F-Co-PBO. An analysis of the dissipation factor DF-temperature profiles of the three polymers revealed the following. FDAPE film showed the lowest DF among the films tested, with the DF increasing from 0.08 % at RT to 0.12 % at 350°C. In the case of FPE, the DF was found to fluctuate in the 0.3 %-0.6 % range. For the 6F-Co-PBO film, DF was found to increase threefold from 0.3 % at RT to 0.9 % at 350°C. Interesting variations in wide-temperature insulation resistance characteristics were also observed for the different polymer films in the RT-350ºC range. In the case of FPE, there was an overall decrease in volume resistivity by nearly four orders of magnitude from 1.2 x 10^{17} ohm.cm at RT to 3.2 x 10^{13} ohm.cm at 350ºC. 6F-Co-PBO showed resistivity decrease from 2.7 x 10^{15} to 3 x 10^{13} ohm.cm and FDAPE exhibited considerably less variation in volume resistivity, with a decrease from 1.7 x 10^{17} to 8.7 x 10^{16} ohm.cm in the entire RT-350ºC range. The high temperature insulation resistance of FDAPE was the highest among the three polymer films tested and compared well with the RT values of IR reported for Teflon film.

From the viewpoint of energy storage considerations, RT dielectric breakdown measurements were performed on the polymer films with 3 mm Al electrodes which were already subjected to high temperature LCR measurements. Average room temperature breakdown strengths for 6F-Co-PBO and FDAPE films ranged from 240 to 245 V/µm while it was measured to be 440V/µm under the same experimental conditions for the FPE film. However, optimization of the current

solvent–based laboratory scale thin film fabrication process can lead to potentially higher film breakdown strengths for both FDAPE and 6F-Co-PBO films.

2.0   Introduction and Background

The development of compact, mechanically robust, thermally stable, high energy density capacitors is widely acknowledged as a technology driver for future high-temperature, high-power electronic systems but has many challenges to overcome [1]. Increasing proximity of electrical components (e. g., capacitors) to heat sources poses thermal management issues to the Power Electronics systems; thus new design criteria should be geared towards enhancing the reliability of the power system by efficiently decreasing the thermal load for the cooling system for the electronics. Aerospace capacitors can occupy up to 30 % of the volume in power systems and have been identified as the limiting component in certain applications requiring stability as a function of both temperature and frequency. A substantial improvement in the required characteristics will thus have a notable impact on furthering the development of more robust electrical power systems with increased power density, performance, and reliability.

The following performance criteria have to be met for fulfilling the Department of Defense (DoD) requirements for wide-temperature Air Force power electronics applications.

- The temperature range of stable operation from -55ºC to 250ºC or greater. This would require the variable temperature film capacitance to be stable as indicated by a low temperature coefficient of capacitance (TCC) (preferably < 5 %) over the entire temperature change.

- A low dissipation factor of the order of 0.01 % -0.1 % (0.0001-0.001) at frequencies of interest (1kHz and 10 kHz frequencies).

- High insulation resistance (IR) over the entire temperature range for the utilization of the thermally stable dielectrics not only for power system conditioning capacitor applications but also for wiring insulation and passivation of electronic devices.

- Ideally, an energy density capability of 10 J/cc (~4 J/cc when packaged). Recommended approach should consider achieving such a target via high breakdown strength (> 500 V/μm) of a thin dielectric film (< 5 μm) or with a thicker film possessing a dielectric constant (k > 5).

- Either rolled or stacked architecture of the device may be considered, depending upon the application, but the device needs to have a graceful failure mechanism. In other words, the gradual failure of these devices will result in a steady decrease in capacitance over time, which can be detected and replaced before catastrophic failure. This modular replacement capability will enhance mission safety, predictability, and capability.

- Last but not least, the ultimate device should also exhibit a low parasitic inductance to operate reliably at high frequencies up to 500 kHz.

High temperature polymer films comprise a class of dielectric materials suitable for wide-temperature capacitor applications because of their inherent potential for high dielectric breakdown strengths, low dissipation factors and good dielectric stability over a wide range of frequencies and temperatures. Besides being lightweight, they are also amenable to continuous, large area fabrication into thin films at a relatively lower cost and this is an important consideration for manufacturing/testing of capacitors. An added advantage of a metalized polymer thin film capacitor design is its 'self-healing' or 'clearing' capability [2, 3] to ensure a graceful failure mechanism. Other capacitor devices (e. g., ceramic and electrolytic) are known to fail in a catastrophic manner. It has to be generally recognized, however, that the volumetric/gravimetric energy density of a capacitor based on polymer films is driven more by dielectric strength considerations rather than their relative permittivity [4]. The following Table describes a range of commercial polymer films which have been considered or evaluated as dielectrics for capacitor applications.

Table 1. Dielectric Properties of Various Available Polymer Films*

Properties	Units	PC	PEN	PPS	PI	PTFE	FPE**
Dielectric Constant (1kHz)	-	3	3.2	3.1	3.3	2	3.3
Dissipation Factor (1kHz)	%	0.1	0.5	0.06	0.2	0.01	0.03
Breakdown Strength	kV/mil	9	12	10	10.5	4.2	10
Resistivity	$\Omega \cdot$cm	10^{16}	10^{15}	10^{16}	10^{17}	10^{19}	10^{17}
Moisture Absorption	%	0.3	0.4	0.05	2.5	<0.1	1.3
Max Use Temperature	^{o}C	125	135	150	>300	260	275
Available Thicknesses	μm	2-20	2-20	2-10	>50	9-20	4-10

* (Reference 5 in this report) Mark A. Carter, *Power Electronics Technology*, **2002**, 31.
** Ferrania Technologies, reported FPE film properties

One of the DoD criteria that need to be clearly met is the capability of the capacitors to withstand repeated thermal cycles during operational use. The dielectric stability of the device determined by a low temperature coefficient of capacitance, as well a low temperature-dependent dissipation factor at the higher temperatures, is strongly correlated with the thermal and thermo-mechanical characteristics of the polymer films. Also, as a function of increasingly applied electrical stress, a metalized polymer film undergoes localized joule heating which presumably arises from high leakage current, causing the temperature within the dielectric to rise well above its glass transition temperature. This is considered to be responsible for the electro-mechanical degradation of the polymer film. High glass transition temperature of polymer dielectric films may help delay the initiation of electro-mechanical breakdown under an applied electric field. It has been suggested that a correlation exists between film electrical breakdown and its mechanical properties when the temperature reaches the softening point [6].

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Polycarbonate (PC) capacitor grade film is commonly referred to as a benchmark dielectric for fabricating power conditioning capacitors. PC has a reasonably low DF of 0.1 % at 1 kHz and a film dielectric strength of ~ 360V/µm but is limited for use in the temperature range of -55ºC to 125ºC. This falls far short of AF-identified requirements for utilization in power conditioning capacitors under temperatures exceeding 250ºC or even 300ºC. Polyethylene naphthalate (PEN) polyester has a relatively high dielectric strength approaching 500 V/µm and a moderately low DF (0.5 % at 1 kHz) but is still limited by use temperatures up to only 135ºC. For higher operating temperatures up to 200ºC, capacitors incorporating semi-crystalline poly(p-phenylenesulfide) (PPS) films have been evaluated [5] because of their low DF (0.06 % at 1 kHz) and good dielectric strengths approaching 400 V/µm. Interestingly, Kapton polyimide (PI) is a polymer film with a reported use temperature > 300ºC and has some desirable dielectric properties; however, its main drawback is a relatively high moisture absorption that results in problems such as arc tracking during use as a high temperature insulator. Poly tetrafluoroethylene (PTFE) has a very low DF (0.01 % at 1 kHz), a very high resistivity (insulation resistance), as well as a relatively high use temperature but has a low dielectric strength as well as a very low dielectric constant making it unsuitable for energy storage applications. Besides, PTFE is also difficult to handle in roll-to-roll processing as well as to metalize. Kapton has a similar drawback; it cannot be fabricated into films thin enough for attaining required volumetric efficiency for power conditioning capacitor applications. Recently, amorphous high temperature fluorenyl polyester (FPE), which has been originally researched for space power conditioning [7], is also being touted as a potential replacement for PC in aerospace power conditioning applications. FPE has a relatively high dielectric strength (400 V/µm) as a thin film, a dielectric constant of 3.3 and a reported low dissipation factor of 0.03 % at 1 kHz and a maximum operating temperature in the 250-275ºC range. However, long-term ≥ 300ºC thermal endurance requirements for future power conditioning capacitor applications as well as the fact that FPE film is not currently manufactured in the United States necessitate more research and development in the area of high temperature polymer dielectrics for reliable operation in AF wide-temperature power electronics.

The research described in this report is geared primarily toward the tailorable design, development, thin film fabrication and dielectric evaluation of high performance polymer dielectrics for utilization in AF wide-temperature power electronics applications. The major focus of the investigation has been on the temperature dependence of film dielectric properties such as capacitance (or dielectric constant), dissipation factor and insulation resistance. Two main tasks were pursued to accomplish this objective. The first one consisted of wide-temperature dielectric evaluation of a broad range of thin films fabricated from high temperature polymer systems ranging from polyimides to polybenzoxazoles. In the second task, polymer candidates were down selected specifically for wide-temperature evaluation up to 350ºC or even higher and the focus was on the influence of thermal cycling on the film dielectric stability. The variable temperature dielectric properties of the candidate films were compared with those of the state-of-the-art commercial FPE films, measured under the same experimental conditions. Besides the variable temperature LCR studies, the film dielectric strengths of the various films were also measured and reported. Recommendations for potential utilization of the high temperature polymer dielectric films in AF power conditioning as well as in other power system applications are also provided in this report.

3.0 Methods, Assumptions, and Procedures

3.1 High Performance Polymers Utilized as Dielectrics in this Program-General

The synthesis of the fluorinated polybenzoxazole (OH-6F-PBO/12F-PBO copolymer, referred to as 6F-Co-PBO in the text) has been described elsewhere in the context of micro-electronics applications [8]. Synthesis of a fluorinated hydroxyl-pendent polyimide as well as that of PI-ADE (polyimide containing adamantyl ester pendant) derived from the post-polymer reaction of the hydroxyl polyimide (PI-OH) with adamantane-1-carboxylic acid chloride have also been described recently [9]. The synthesis and characterization of the cardo-type polyester FDAPE has also been reported in recent AFRL studies [10, 11]. Preliminary findings on the variable temperature dielectric properties of a range of high performance polymer films from AFRL have been reported elsewhere during the course of this program [12]. FPE films, provided by Brady Worldwide Coatings, Inc., to AFRL/RZPE, were evaluated for comparison. Besides the films described above, a polyphenylquinoxaline (PPQ) polymer obtained from Akron polymer Systems, Akron, OH, was also evaluated as a thin film dielectric. Polyphenylquinoxalines are polymers with high thermal and thermo-oxidative stabilities and their evaluation as thermostable capacitor films has been described in the patent literature [13].

The thermal and thermo-oxidative stabilities of the polymer in both powder and film form were determined by Thermo-Gravimetric Analysis (TGA) and the glass transition temperatures of the polymer powder were determined by DSC (differential scanning calorimetry).

3.1.1 OH-6F-PBO/12F-PBO Copolymer or 6F-Co-PBO

The polymer utilized in this study is a 50/50 random copolymer consisting of a 6F-polybenzoxazole with a hydroxyl pendant as well as a 12F-polybenzoxazole unit. The particular batch was derived from the scaled up custom synthesis efforts of Tristate Chemicals, Dayton, OH. For the purpose of fabricating dielectric films, the bulk polymer was dissolved in tetrahydrofuran (THF) and the polymer was reprecipitated in heptane non-solvent. The filtered polymer was washed with heptane and was finally dried in vacuum at 100ºC for three days to obtain the dry polymer. The intrinsic viscosity of the polymer, measured in methanesulfonic acid (MSA) at 30ºC, was 1.1 dl/g.

3.1.2 Fluorenyl Polyester with 4,9-Diamantyl Unit (FDAPE)

One of the monomers, 4,9-diamantanediacid chloride was prepared as follows. 4,9-Diamantanedicarboxylic acid (3 gms) was refluxed for 3 hours with an excess (60 ml) of thionyl chloride in presence of a few drops of N,N-dimethylformamide (DMF) under a flow of dry nitrogen. The hot, yellow solution was filtered hot and the thionyl chloride was removed in a rotary evaporator. The off-white residue was recrystallized from 300 ml hot heptane. A yield of 2 g was obtained, m.pt., 230-232˚C.

The batch of FDAPE polymer utilized in the wide-temperature dielectric investigation was generated as follows. In a three-necked flask fitted with a magnetic stirrer-bar, a reflux condenser

and a nitrogen inlet, 9,9-bis(4-hydroxyphenyl)fluorene (recrystallized from toluene, 1.0 g, 2.86 m.moles) and 4,9-diamantanediacid chloride (0.894 g, 2.86 m. moles) were mixed with anhydrous 1,2-dichlorobenzene (8 ml) under a dry nitrogen flow. The mixture was heated to a temperature range of 165˚C-170˚C after complete dissolution of the monomers. After 24 hours, the polymerization mixture was cooled to room temperature. The viscous solution was added to a large excess of methanol to precipitate the polymer. After soxhlet extraction with methanol and vacuum drying, the polymer was purified via dissolution in chloroform and reprecipitation in excess heptane. The filtered off-white polymer was dried *in vacuo* at 100˚C for 24 hours. The yield of the polymer was 1.6 g (94 percent). An intrinsic viscosity of 0.66 dl/g was measured for the polymer in N-methylpyrrolidone (NMP) at 30˚C at an initial concentration of 0.25 g/dl.

3.1.3   Fluorinated Polyimide Containing Adamantyl Ester Pendant Group (PI-ADE)

This two-step preparation of polyimide PI-ADE has been described [7]. The first step was the synthesis of the hydroxyl polyimide (PI-OH) precursor to PI-ADE. A typical procedure for the one-pot direct imidization step for PI-OH is as follows.

2,2-Bis(3-amino-4-hydroxyphenylhexafluoropropane) (2 m.mol) was reacted with equimolar amounts of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) in the presence of triethylamine, γ-valerolactone and pyridine with NMP and toluene as solvents. The mixture was heated at 180ºC under nitrogen overnight. After cooling, the polymer was precipitated in methanol/water (1:2 v/v). The PI-OH polymer was filtered and dried in vacuum at 80ºC for 24 h. An intrinsic viscosity of 1.07 dl/g in NMP was measured at 30ºC.

The subsequent functionalization of PI-OH to synthesize PI-ADE was accomplished by a post-polymer reaction utilizing the hydroxyl side-group. A solution of excess adamantane-1-carbonyl chloride (10 mmol) in N,N-Dimethylacetamide (DMAc, 10 ml) was added drop wise to a DMAc solution of the PI-OH polymer (1.5 g) in presence of excess triethylamine (TEA, 10 mmol) as the acid scavenger at 0ºC.   After the mixture was warmed to RT and stirred overnight, the precipitated triethylammonium hydrochloride was removed and the filtrate was added to precipitate the polymer. The polymer (PI-ADE) was filtered and dried *in vacuo* at 80ºC for 24 h. An intrinsic viscosity of 1.17 dl/g was measured at 30ºC in NMP.

3.2   Thermo-mechanical and Mechanical Properties of Polymer Films

The thermo-mechanical properties of 90 μm thick solvent-cast films of 6F-Co-PBO and FDAPE and a 30 μm thick commercial FPE film were investigated by dynamic mechanical analysis (DMA) and thermo-mechanical analysis (TMA).

Glass transition temperatures of the polymer films were determined by both DMA and TMA via tan δ and dimensional change measurements respectively. The storage modulus of the films was also measured in DMA over a wide temperature range. Film mechanical properties such as tensile strength, tensile modulus and elongation-at-break were evaluated using a Tinius tensile tester at a strain rate of 1 mm/min.

3.3 Thin Film Fabrication for Dielectric Measurements

Thin, freestanding polymer films were fabricated by solvent casting. 6F-Co-PBO films were cast from tetrahydrofuran (THF) as solvent while FDAPE films were generated from chloroform solutions of the polymer. PI-ADE films were fabricated from DMAc solutions *in vacuo*. PPQ thin films were fabricated from chloroform solutions. After slow solvent evaporation from the flat glass casting dishes placed inside a desiccator, the thin films were carefully released from the glass dish by the addition of de-ionized, distilled water. The films were dried at ~ 0.1 torr vacuum and 80-85ºC in an oven for several days. Several circular films varying in diameter from 2" to 4" were fabricated and their average film thickness, measured by the thin film measurement system MP-100S (Mission Peak optics Inc.), was typically in the range of 3 µm to 8 µm, with the exception of a few films which had film thickness in the 9-11 µm range. The average thickness of a continuous, roll-to-roll processed freestanding FPE film (Brady worldwide Inc., batch # 157412-A-Y-64290-2) already metalized on one side with 0.1 nm thin aluminum layer, was 5.7 µm.

3.4 Metalized Single Film Device Fabrication

Aluminum top and bottom electrodes with 100 nm thickness were deposited on both sides of the freestanding films using a Kurt J. Lesker thermal evaporator system. For small (2" diameter) dielectric films, circular electrical contacts with 3 mm diameter (7×10^{-2} cm^2 area) were deposited. In the case of larger polymer films (4" diameter), circular aluminum contacts with 2 cm^2 area were deposited. Design of the exact metalized film configuration for standardizing dielectric tests for comparative evaluation with FPE films will be discussed later in this report.

3.5 Dielectric Evaluation of Metalized Films

Film capacitance and dissipation factor were measured using Agilent HP4284A LCR (Inductance Capacitance Resistance) characterization system at frequencies ranging from 20 Hz to 1 MHz with a 1 V AC applied voltage. Variable temperature LCR measurements were conducted in a high temperature test station with operating temperature capability up to 1000ºC. The test station had a 100V/10A power supply, a temperature controller and a vacuum controller. A vacuum of < 1 µ torr was achieved with a combination of a turbo pump and a scroll pump system. The sample probing is accomplished with a three-axis molybdenum probing rod test fixture. The dielectric measurements of the metalized films were conducted up to 350ºC as the upper limit in increments of 50ºC from room temperature. Towards the end of the program, temperature-dependent LCR measurements were also performed up to 400ºC to assess the short-term dielectric stability of some of the high temperature films. While the initial film evaluation studies were confined to one thermal cycle, most of the film dielectric properties in this report were typically monitored over two complete (ramp up and ramp down) thermal cycles. In the case of the some of the high temperature films, the variable temperature dielectric stability was also examined as a function of applied DC bias in the 10 V-40 V range.

While the initial wide-temperature LCR measurements utilized the manual mode of temperature control, measurements in the later stage of the program were performed using the automated LCR High Tmp DAQ Ver 1.0.0.2 Program. Repeated thermal cycling LCR measurements in a relatively short period of time could be performed using this automated LCR program developed by William Lanter, Capacitor Research Group, AFRL/RZPE.

Film insulation resistance (IR) was also measured in the high temperature test station using a Keithley 6517A Electrometer/High Resistance Meter. There was a 100K-Ohm resistor in series with the sample to protect the electrometer input in case of voltage breakdown. A 40 V DC bias was applied to the sample for 60 seconds to charge it, and then the IR/leakage current data were acquired over a 60 s time period. These measurements were also taken at 50ºC intervals from room temperature to 350ºC.

The breakdown strength of the metalized thin film polymer dielectric was evaluated using precision regulated high voltage power supply models Bertan 210-05 R and Spellman SR6 with operating voltage capability up to 5 kV and 30 kV respectively. The current was measured using a Hewlett Packard 4349A 4-Channel High Resistance Meter. There was a 200 Mega-Ohm resistor in series with the sample to protect the meter input during voltage breakdown. The DC voltage was ramped at 50 volt intervals until breakdown.

4.0   Results and Discussion

4.1   Polymer dielectrics used in this study

The chemical structures of the various high temperature polymer film dielectrics used in this study and the synthetic schemes for the preparation of various polymers are shown in Figures 1-4.
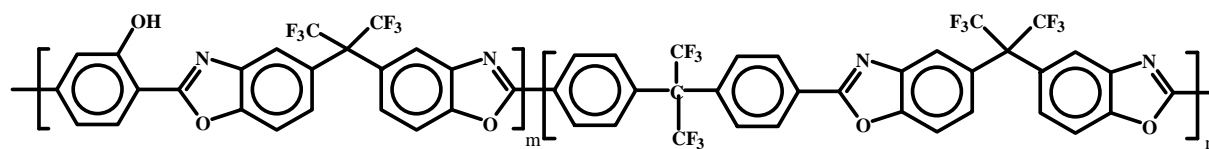
OH-6F-PBO/12F-PBO Copolymer (50/50) or 6F-Co-PBO
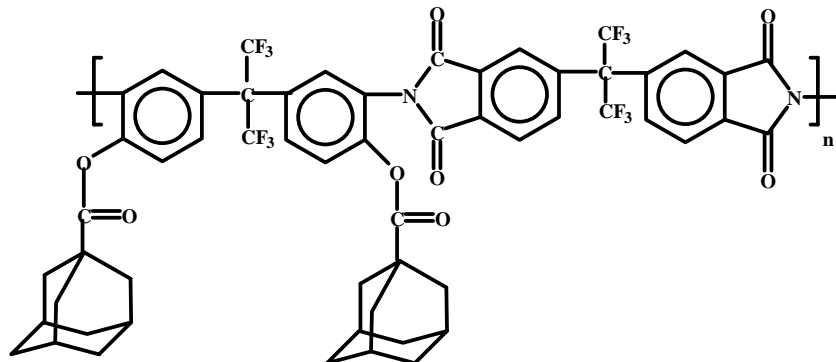
PI-ADE
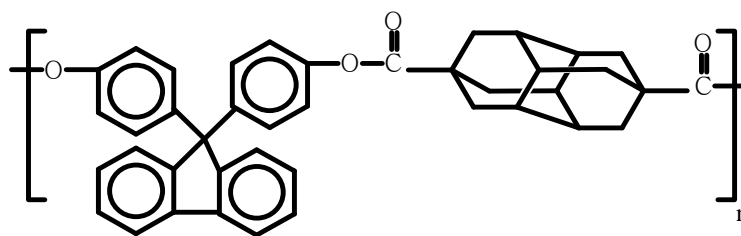
FDAPE

Figure 1. Polymer Film Dielectrics Evaluated For
AF Wide-temperature Power Electronics Applications
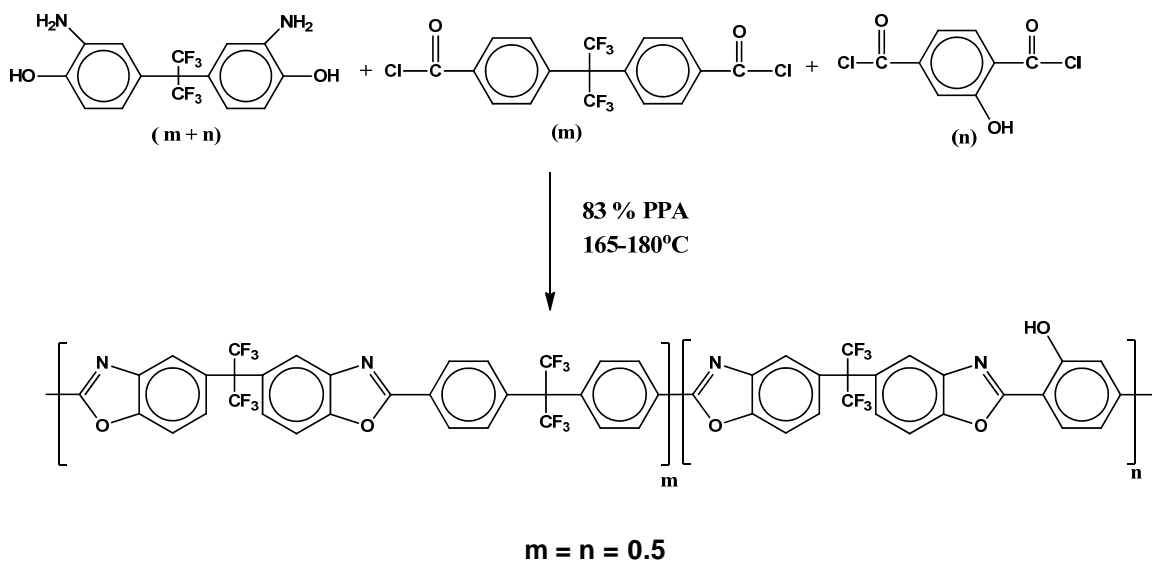
Figure 2. Synthesis of the OH-6F-PBO/12F-PBO Copolymer (6F-Co-PBO)
in Polyphosphoric acid (PPA)

Chemical imidization Conditions:
NMP/Toluene, γ-valerolactone,
Pyridine, 180°C, N₂.

Post-functionalization: 1-Adamantoyl
Chloride, DMAc, 60°C/16 h.
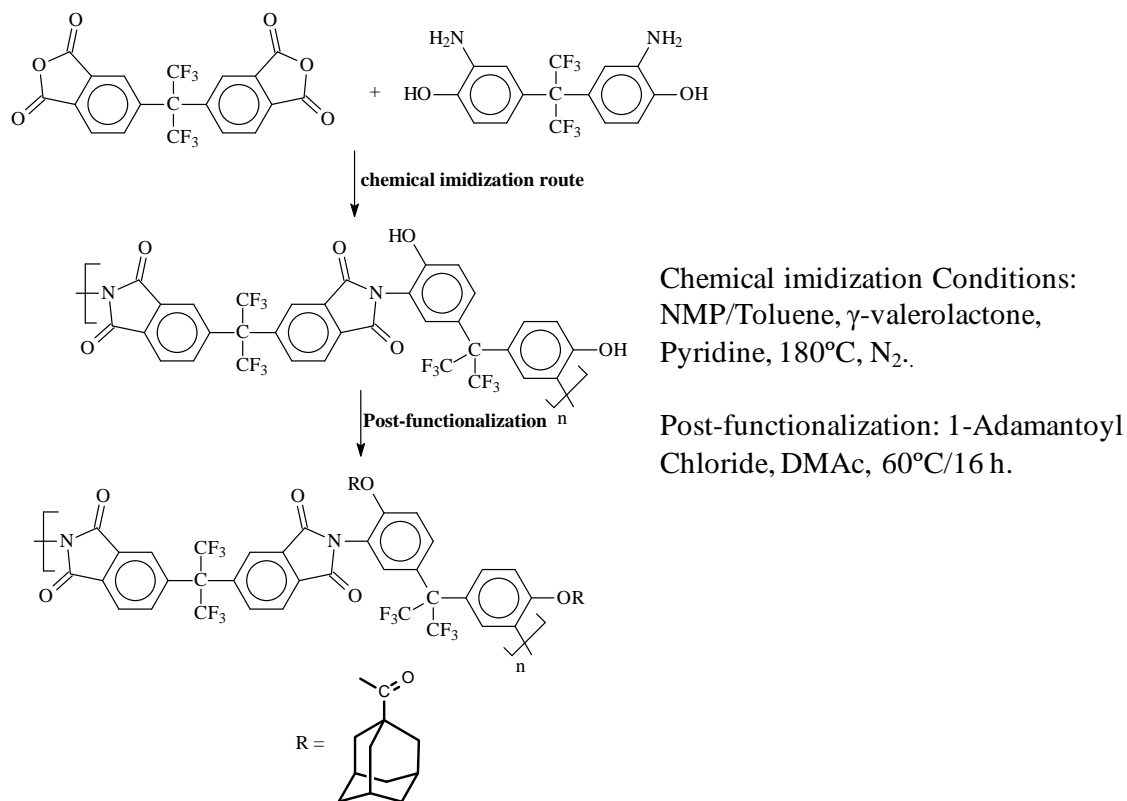
Figure 3. Synthesis of the Fluorinated Polyimide with the Adamantyl Ester Pendant
(PI-ADE) by a Two-step Method

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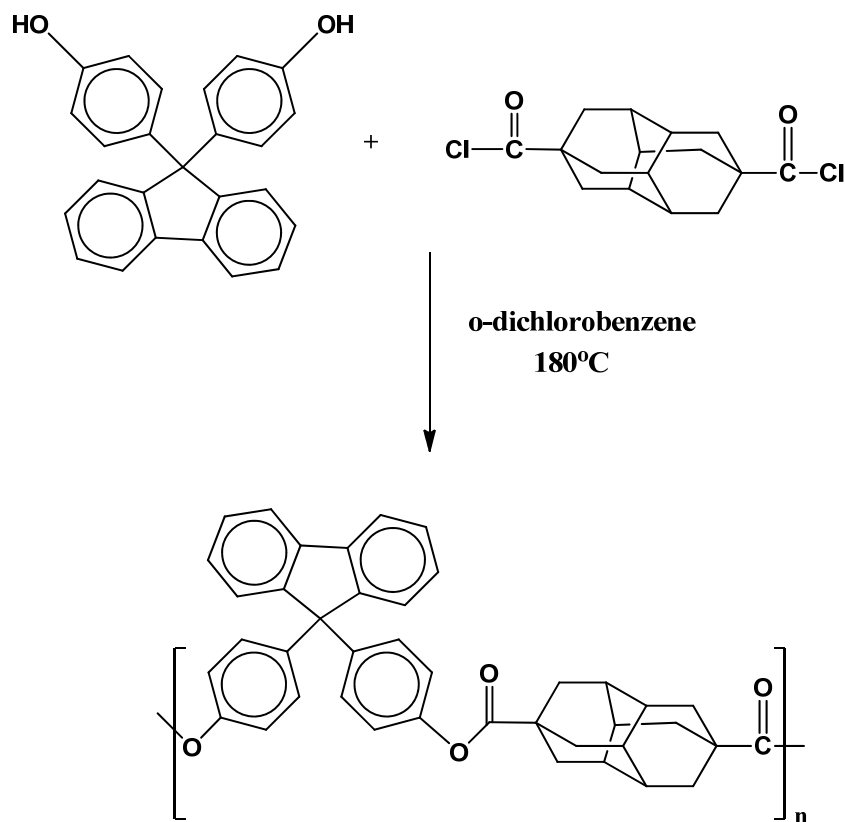
Figure 4. Synthesis of the Fluorenyl Polyester (FDAPE) Examined in this Study

The rationale behind the design of these polymer dielectric structures for wide-temperature power system conditioning capacitors is described as follows. Besides the potential for electro-mechanical stability at high temperatures due to their high glass transition temperatures and thermal stability, some established criteria for micro-electronic packaging applications of fluorinated polybenzoxazoles [8] and fluorinated polyimides [14, 15] are equally important for their dielectric applications in wide-temperature power electronics. The versatility of the hydroxyl pendant in fluorinated polyimides can be utilized to develop novel, tailorable dielectrics such as PI-ADE (Figure 3) by post-functionalization reactions. The incorporation of a diamond-like hydrocarbon unit or diamondoid in the fluorenyl polyester backbone [10, 11] (FDAPE) or as a pendant in the fluorinated polyimide (PI-ADE) structure [9] is expected to enhance film insulation resistance and dielectric strength based on the rationale that the HOMO (Highest Occupied Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbital) band gaps in diamond-like hydrocarbons are molecular counterparts of a large fundamental band gap in diamond itself [16, 17].

4.2   Thermal Properties of the Polymer Systems

High glass transition temperatures (T_g) and thermal stability of the polymer dielectrics are an important prerequisite for electro-mechanical stability of the dielectrics utilized in the power conditioning capacitor systems. Table 2 lists the T_gs and the thermal degradation (T_d) in nitrogen as well as in air, of the polymers under study.

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Table 2. Thermal Properties of the Polymers in this Study

Polymer	Glass Transition Temperature $(T_g, ^oC)$*	Thermal Degradation $(T_d, ^oC)$, Onset*	
		In nitrogen	In air
OH-6F-PBO/12F-PBO (6F-Co-PBO)	362	525	500
PI-ADE**	305	400	350
FDAPE	>400	450	400

* DSC and TGA of the bulk polymer, ** DMA (tan δ) of the solvent cast film

The glass transition for FDAPE powder was not observed in the DSC scan in the RT-400ºC range. However, the precise determination of the T_gs of both FDAPE and 6F-Co-PBO in the film form using DMA and TMA will be described later in a subsequent section, in the context of their comparison with the commercial FPE films. The > 400ºC glass transition temperature of FDAPE can be ascribed to the presence of the relatively stiff 4,9-diamantane structural unit in the fluorenyl polyester backbone. Among the three polymer systems examined, the fluorinated benzoxazole copolymer had the highest thermal as well as thermo-oxidative stability.

In the case of PPQ (the chemical structure is shown below), the glass transition temperature was relatively low (206ºC) but the thermal and thermo-oxidative stabilities were quite high, with the onset of thermal degradation occurring around 425ºC in both nitrogen and in air.
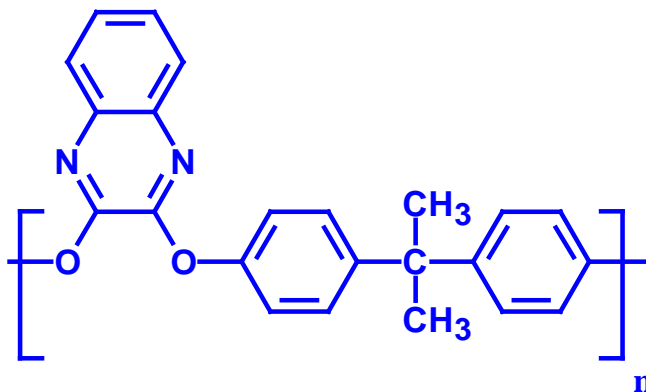
Chemical structure of PPQ evaluated in this study

4.3   Polymer Film Fabrication Techniques

As stated in the experimental section, circular thin films with film thickness in the 3-8 μm range were solution-cast from solvents such as THF, chloroform and DMAc. It is generally recognized that compared to melt processed films, solution-cast films may lead to more morphological defects such as pin-holes. However, optimization of the solvent-based film fabrication process may lead to relatively uniform, defect-free thin films as in the case of continuous, roll-to-roll production of FPE films by Brady Worldwide Inc. Besides, melt processing of the polymers is not generally amenable to fabrication of very thin films, unless they are stretched in the extrusion process [18]. In addition, the high glass transition temperatures of the polymers described in the study (305-450ºC) preclude the option of melt processing the polymers into films. The advantages of the solvent cast thin film technology include uniform thickness distribution, low haze and a virtually isotropic optical orientation [18].

The solvent cast thin dielectric films utilized in this study were optically transparent, ductile and displayed good mechanical integrity and dimensional stability.

4.4   Dielectric Film Characterization

After metalization, the dielectric properties of the films were characterized, with regard to their variable temperature capacitance, dissipation factor as well as insulation resistance. Room temperature DC breakdown voltage measurements were also performed on the films.

4.4.1. Variable temperature film capacitance and dissipation factor

Among the screening tests performed to assess the dielectric stability of the metalized polymer films as a function of temperature, the primary measurements were those of film capacitance and DF, from room temperature up to maximum temperatures in the range of 250-350ºC. TCC, expressed as % change in film capacitance at any given temperature relative to room temperature, is the signature of wide-temperature dielectric stability for capacitors. The maximum temperature for testing was determined by the glass transition temperature (T_g) of the polymer which would limit the dimensional and electro-mechanical stability of the dielectric. Typically, these films were initially tested up to temperatures which were 50-100ºC below their T_gs to ensure dimensional stability during measurements. The high temperature LCR testing station and the metallized freestanding films with 3 mm and 2 cm^2 circular aluminum electrodes are shown in Figure 5 (a & b). The results discussed in this section are mostly based on dielectric measurements performed on metalized polymer films with 3 mm circular Al electrodes.
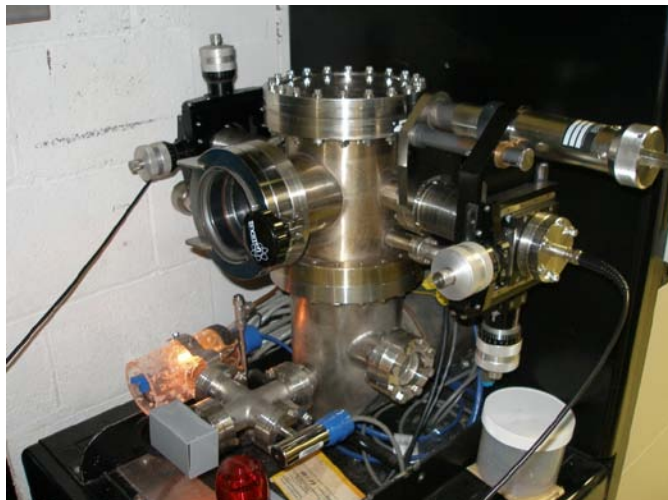
(a)

(b)

Figure 5. Variable Temperature Dielectric Evaluation (a) High Temperature LCR Testing Station and (b) Metalized Polymer Films

Since the PPQ utilized in this study had a relatively low T_g (206ºC), the variable temperature LCR measurements were performed in the RT-150ºC range. In this case, a PPQ film with a deposited metal electrode area of 2 cm^2 was examined.

4.4.1.1 Initial studies-6F-Co-PBO and PI-ADE thin film evaluation

Initial temperature-dependent film dielectric properties were measured in the RT-250ºC range. The metalized film was tested, under high vacuum (< 1 µ Torr), in the high temperature LCR test station with respect to its capacitance and dissipation factor. Figure 6 (a) shows measured film capacitance (in pico-Farads, (pF)) as a function of frequency over the temperature range in increments of 50ºC during the ramp up cycle. Figure 6 (b) depicts the corresponding % change in film capacitance at the measurement temperature relative to the room temperature value.
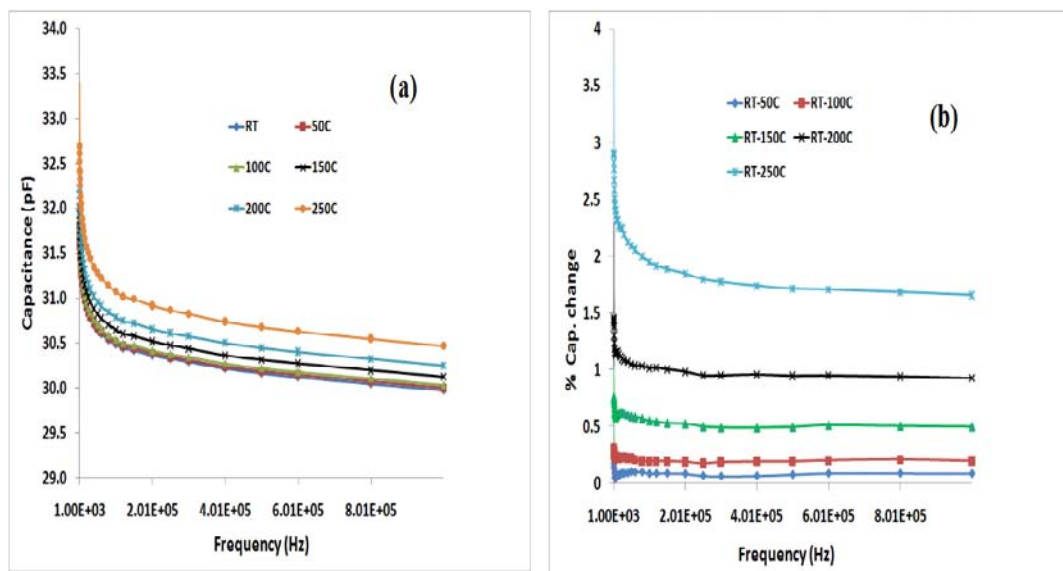
Figure 6. Variable Temperature Dielectric Studies (a) Capacitance of 6F-Co-PBO Polymer Film and (b) the Corresponding % Capacitance Change at Different Temperatures

Small incremental changes in film capacitance were measured as a function of temperature and the steady capacitance value over a large frequency range was found to increase by ~ 2 % in the RT-250ºC range. This corresponds to a change in film capacitance of ~ 88 ppm/ºC, demonstrating the desired stability of the dielectric over the wide temperature range. Capacitance measured over a complete heating (RU) and cooling cycle (RD) at the frequency of interest for power conditioning capacitor applications (10 kHz) shows a slight hysteresis effect (Figure 7 (a)). Thermal history as well as the film coefficient of thermal expansion (CTE) in the temperature range of RT-250ºC has to be considered in explaining the small, measured changes in film capacitance. A room temperature dielectric constant of 2.95 at 10 kHz was derived for the copolymer film from the measured capacitance. A similar hysteresis effect was also observed during the complete thermal cycle for the measured film dissipation factor DF (Figure 7 (b)). Over a complete thermal cycle in the RT-250ºC range, an increase in DF from 0.014 to 0.017 was noted. While a gradual increase in film dissipation factor was evident, no sharp region of increased dielectric loss was noticed since the highest temperature of measurement was well below the polymer glass transition temperature.
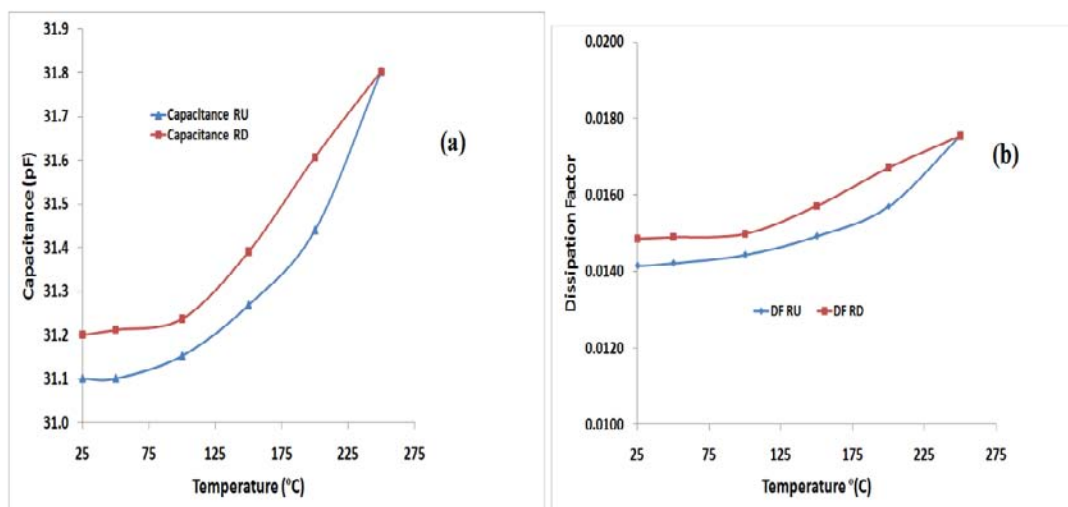
Figure 7. Dielectric Studies (a) Film Capacitance and (b) DF as a Function of Temperature for the 6F-Co-PBO Polymer at 10 kHz Frequency

The metalized PI-ADE film was also tested in the temperature range of RT-250°C. The measured film capacitance at various temperatures as a function of frequency is shown in Figure 8 (a). The high temperature dielectric stability of the film was indicated by minimal changes in the measured values of film capacitance relative to the room temperature value. The observed capacitance variation of ~ 2 % over the entire temperature range (Figure 8 (b)) is similar to that of the 6F-Co-PBO copolymer film. A relatively sharp increase in film capacitance, observed at 250°C, in comparison to capacitance at the lower temperatures, can be tentatively attributed to the proximity of the measurement temperature to the polymer T_g of 305°C. Film dielectric constant, invariant over a large frequency range, was derived from the film capacitance based on a circular electrode of 3 mm diameter and a mean dielectric film thickness of 7.6 µm and ranged from 2.85 to 2.91 in the RT-250°C region.

As in the case of the 6F-Co-PBO film, a slight hysteresis effect was observed in measured film capacitance at 10 kHz frequency (Figure 9 (a)) over a complete thermal cycle. The measured film dissipation factor at 10 kHz (Figure 9 (b)) ranged from 0.005 (0.5 %) to 0.008 (0.8 %) for a complete thermal cycle in the RT-250°C range. Relatively sharp variations in film DF were found to occur at 200°C and above.
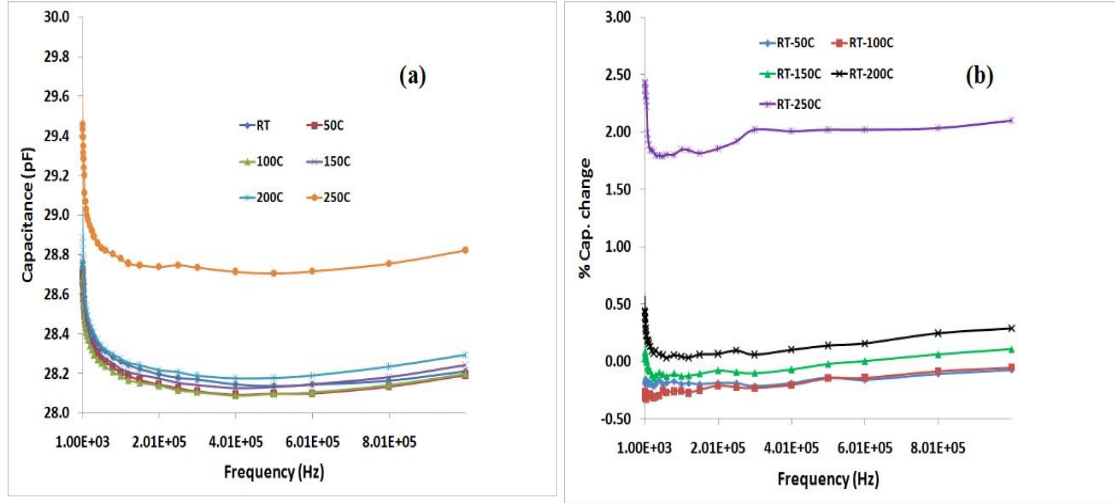
Figure 8. Variable Temperature Dielectric Studies (a) Capacitance of PI-ADE Film and (b) the Corresponding % Film Capacitance Variation
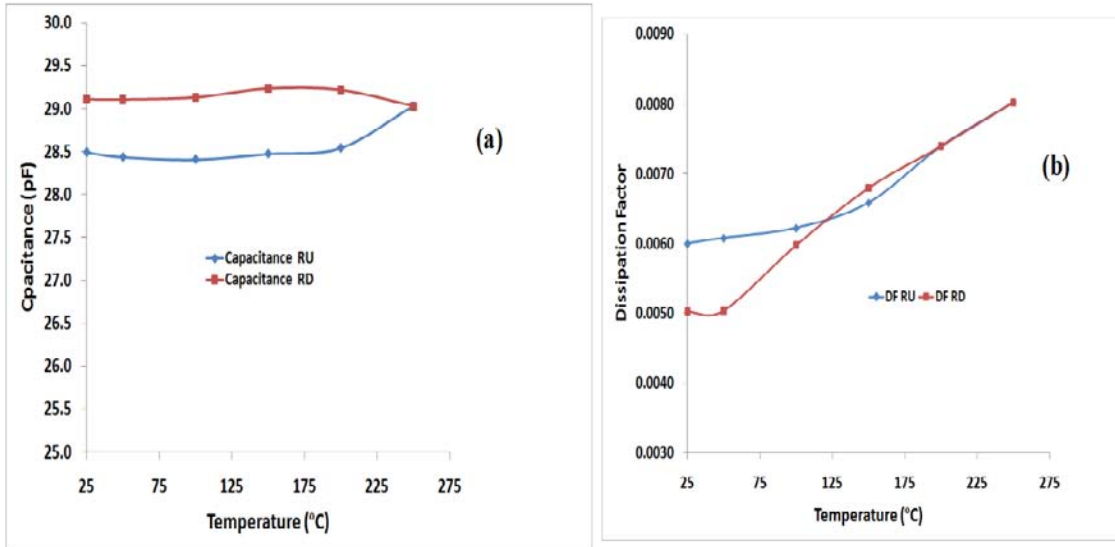
Figure 9. Dielectric Studies (a) Film Capacitance and (b) DF Measured as a Function of Temperature for PI-ADE Film at 10 kHz Frequency.

4.4.1.2 Wide-temperature film dielectric evaluation at > 250°C environment

To further explore the effect of film thermo-mechanical properties on high temperature film dielectric stability at temperatures closer to polymer glass transition, the dielectric properties of the metalized 6F-Co-PBO and FDAPE films were monitored up to 350°C in the current program [19]. Changes in the film capacitance of 6F-Co-PBO at 10 kHz, expressed in pF, were monitored over two complete thermal cycles (Figure 10). The corresponding variations in film dissipation factor (expressed as %) were also monitored (Figure 11). While a marked increase in

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measured film capacitance and dissipation factor were indicated at 350°C, consistent reversion to lower values occurred during the cooling cycles, showing that no degradation of the dielectric had occurred due to thermal cycling in the RT-350°C range. The sharp variations in the film dielectric properties measured at 350°C could be tentatively attributed to the proximity of the operating temperature to the glass transition temperature of the polymer film (375ºC). Also, the decreasing trend in both capacitance and DF with successive thermal cycles is different from what was observed in the RT-250°C range for 6F-Co-PBO (Figure 7). The observed difference in temperature-dependent dielectric behavior may be due to the higher temperature range chosen in this experiment.
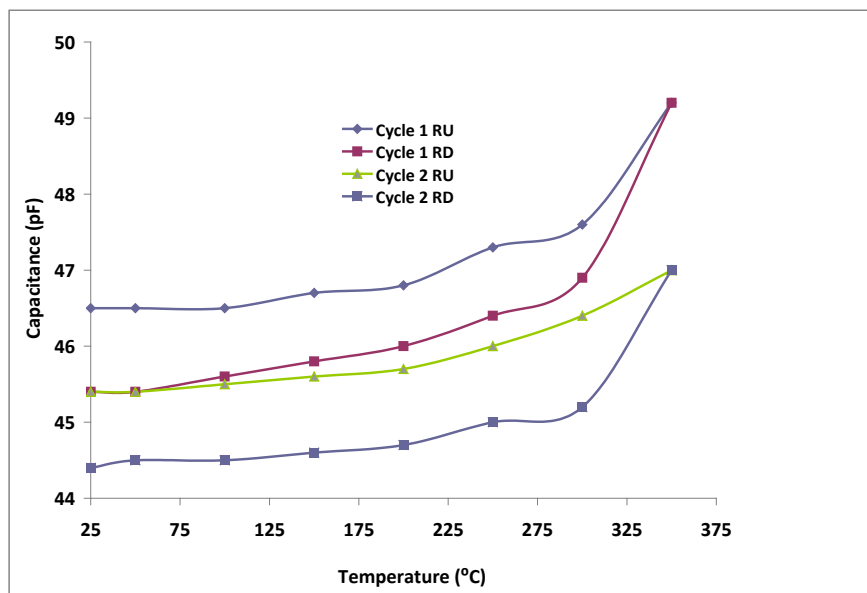
Figure 10. Film Capacitance (Measured at 10 kHz) over Two Complete Thermal Cycles up to 350°C for the 6F-Co-PBO Dielectric
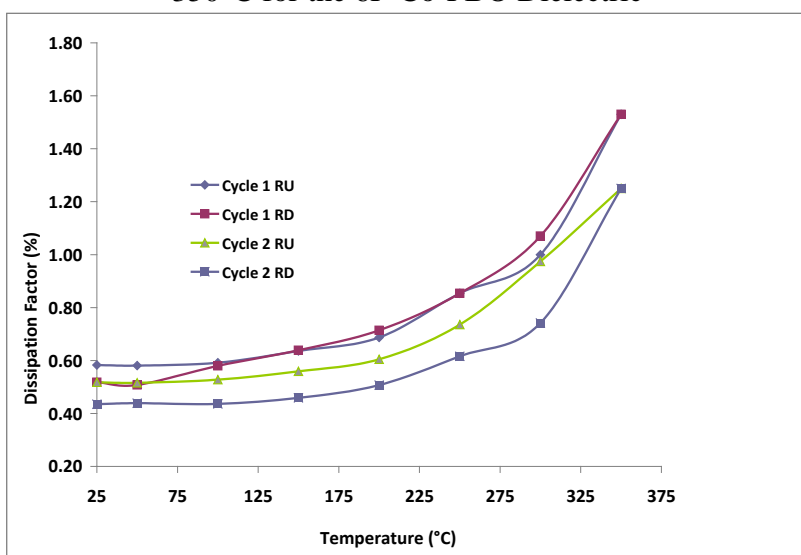
Figure 11. Dissipation Factor (Measured at 10 kHz) over Two Complete Thermal Cycles up to 350°C for the 6F-Co-PBO Dielectric

The dielectric stability of the metalized FDAPE polyester film was examined up to a maximum temperature of 350ºC over two complete thermal cycles. While the first heating and cooling cycles in the RT-350ºC temperature range resulted in fluctuations of 1.9 % to 1.5 % in the measured capacitance values, even lower fluctuations were observed during the second heating (0.8 %) and cooling (0.4 %) cycles (Figure 12 (a)). The film dissipation factor, measured at 10 kHz as a function of thermal cycling, is shown in Figure 12 (b). While the overall changes in DF were not significant, the room temperature dissipation factor was < 0.003 (0.3 %) after the second ramp down experiment. This is somewhat close to dissipation factors of ≤ 0.001 (0.1 %) desired for μs discharge rates in power conditioning capacitors. FDAPE thus displays excellent wide-temperature dielectric stability due to its low TCC up to 350°C; its relatively low DF can be attributed in part to the presence of the 4,9-diamantyl structural unit in its polymer backbone. This will be further confirmed by comparative wide-temperature dielectric evaluation of FDAPE and FPE films, as will be discussed in a later section. It is also seen from Figures 10-12 that changes in DF approximately parallel those of measured capacitance as a function of thermal cycling. This correlation is to be expected since DF =ω.C.ESR where ω is the frequency, C the capacitance and ESR the Equivalent Series Resistance that simplifies to parallel resistance R_p for a capacitor with a low dielectric loss [20].
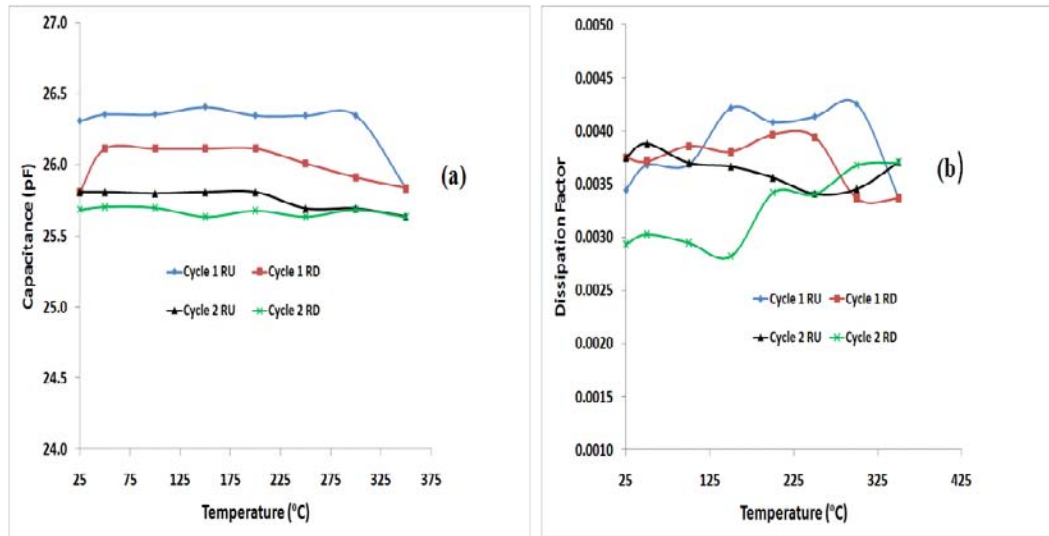
Figure 12. Dielectric Studies (a) Film Capacitance and (b) DF (Measured at 10 kHz) over Two Complete Thermal Cycles up to 350°C for the FDAPE Dielectric

The dielectric stability of the FDAPE film in this temperature range was also reflected in minimal variations in the derived values of the dielectric constant k (3.48-3.51) of the film (Figure 13, RU2 and RD2 refer to heating and cooling in the second thermal cycle). Also, the limited change in k with frequency can be explained by the dominant dielectric mechanism of electronic polarization which is stable over a large range of applied frequencies [6].

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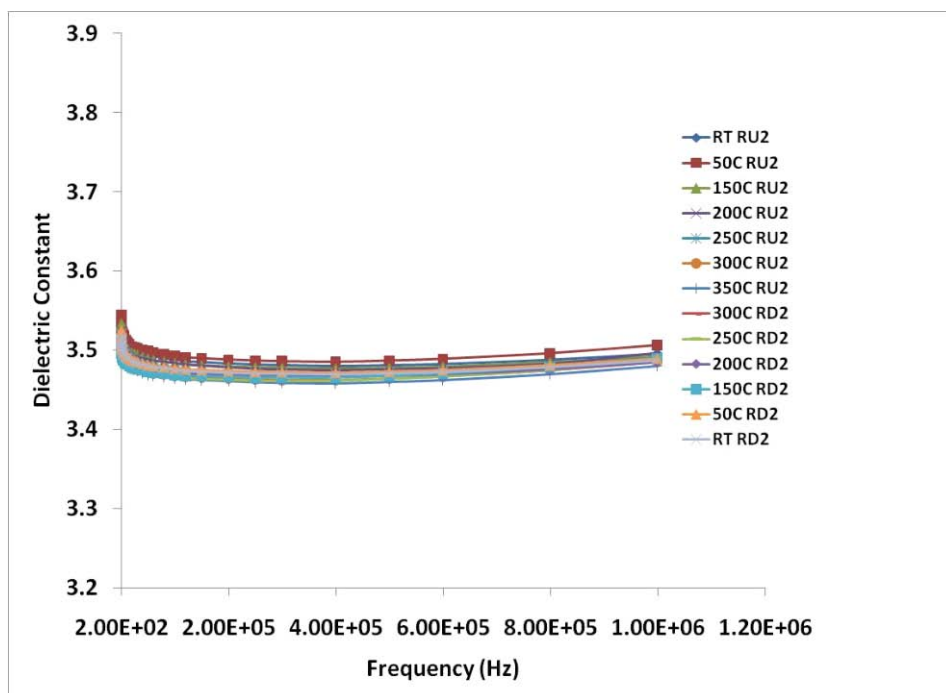
Figure 13. FDAPE Film Dielectric Constant Variations during the Second Thermal Cycle

4.4.1.3 Variable temperature dielectric measurements-metalized PPQ film

The variable temperature film capacitance and the derived dielectric constant of PPQ over two complete thermal cycles in a wide frequency range are shown in Figures 14 (a) and (b). The measured capacitance was found to fluctuate over a range of 671-675 pF (< 1 % overall variation in capacitance) over two complete cycles and the dielectric constant ranged from 2.89-2.91 at the same frequency. They reveal very small to negligible variations in the RT-150ºC range, indicating excellent wide-temperature dielectric stability for the PPQ film.
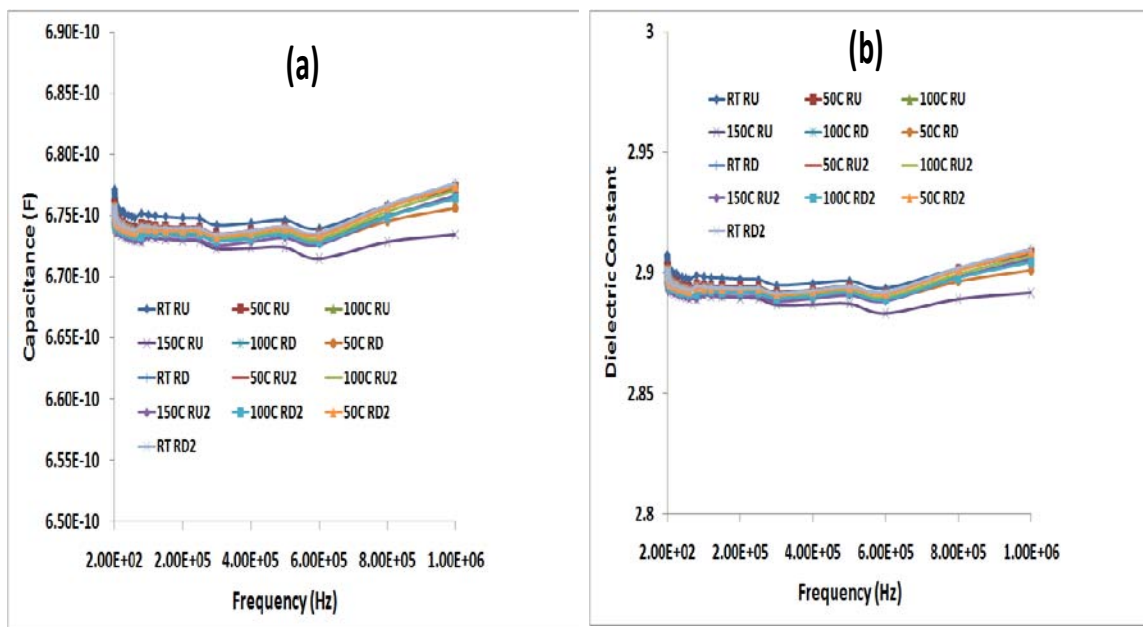
Figure 14. Variable Temperature Dielectric Studies (a) Film Capacitance and (b) Dielectric Constant of PPQ Film over Two Complete Thermal Cycles

The measured DF of PPQ film as a function of temperature in the RT-150°C range over two complete thermal cycles is shown at 1 kHz and 10 kHz frequencies (Figure 15 (a) and (b)). While the DF ranges from 0.1 % (0.001) to 0.15 % (0.0015) at 10 kHz during the first cycle, much smaller fluctuations from 0.1 % (0.0010) to 0.11 % (0.0011) were found to occur during the second thermal cycle. The DF measured at 1 kHz frequency was even lower, ranging from 0.075 % (7.5 x 10^{-4}) to 0.085 % (8.5 x 10^{-4}) and again, the variations during the second thermal cycle are even smaller. This observation points to the stabilization of PPQ dielectric properties with repeated thermal cycling.

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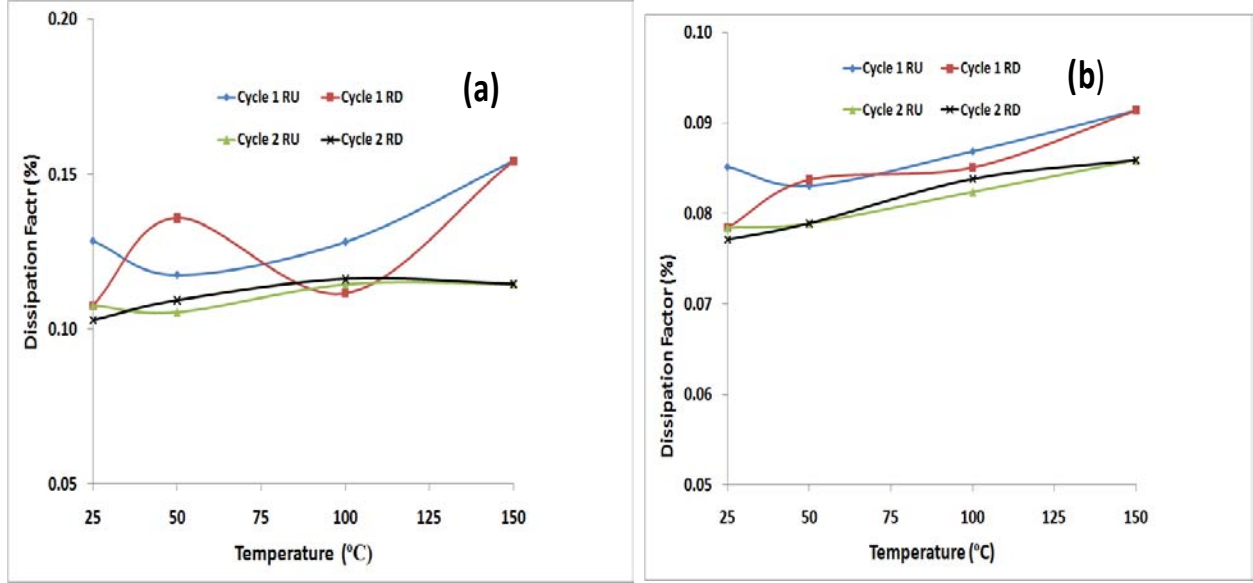
Figure 15. Measured DF vs. Temperature for PPQ Film at (a) 10 kHz Frequency
and (b) 1 kHz Frequency

4.4.2 Preliminary Film Insulation Resistance Measurements

The leakage currents of metalized 6F-Co-PBO and FDAPE films (with 2 cm^2 electrodes and 3 mm electrodes respectively) were also measured in the RT-300ºC and RT-350ºC temperature range using 40V DC as the test voltage and over 60s acquisition time. The derived insulation resistance, expressed as volume resistivity (ohm.cm) was monitored over two complete thermal cycles and the results are shown in Figure 16 and Figure 17 respectively.
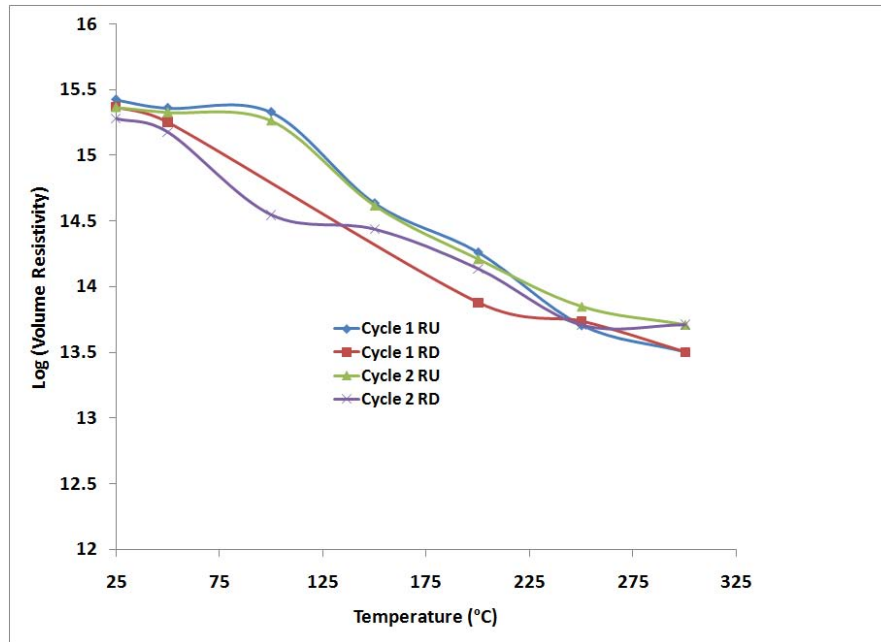
Figure 16. Insulation Resistance of a Metalized 6F-Co-PBO Film as a Function of Thermal Cycling in the RT-300ºC Range
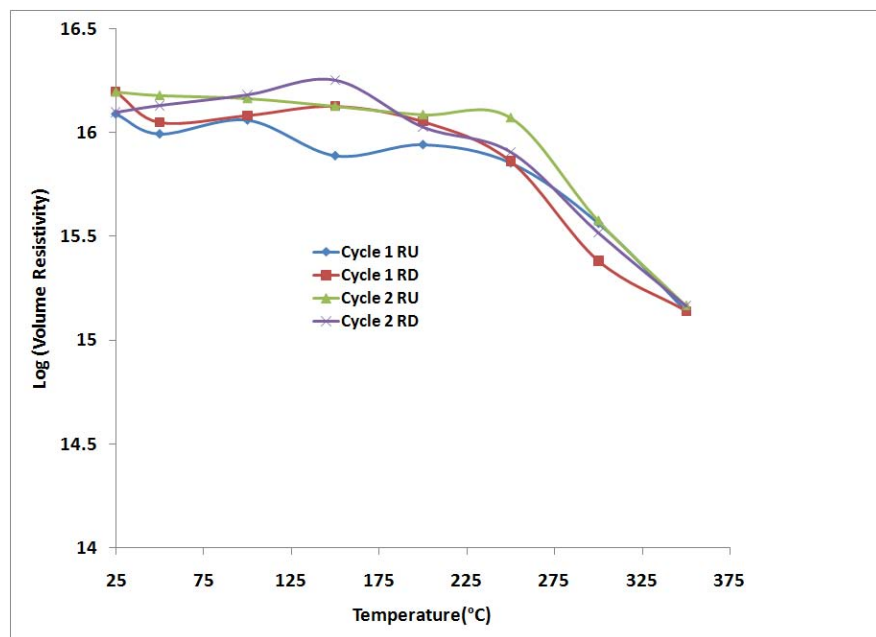
Figure 17. Insulation Resistance of a Metalized FDAPE Film as a Function of Thermal Cycling in the RT-350ºC Range

The variable temperature IR was found to change by nearly two orders of magnitude

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(from 10^{15} Ω.cm at RT to 10^{13} Ω.cm at 300ºC) in the case of 6F-Co-PBO film. In the case of FDAPE film, volume resistivity decreased by just one order of magnitude, from 10^{16} Ω.cm at RT to 10^{15} Ω.cm at 350ºC. The RT resistivity of the films after two complete thermal cycles varied very little from the initial resistivity shown in the following Table (Table 3).

Table 3. Variable Temperature IR (Volume Resistivity) of 6F-Co-PBO and FDAPE Films

Polymer Film	RT Resistivity (Ω.cm), initial	RT Resistivity (Ω.cm), after first thermal cycle	RT Resistivity (Ω.cm), after second thermal cycle
6F-Co-PBO	3×10^{15}	2.3×10^{15}	1.9×10^{15}
FDAPE	1.2×10^{16}	1.6×10^{16}	1.3×10^{16}
FPE (Ferrania)*	$(1\text{-}2.5 \times 10^{17})$	----	----

*Commercial film, reported.

The measured room temperature resistivity of the films was also compared with the RT resistivity of FPE (commercial film from Ferrania) which is reported to be in the 10^{17} Ω.cm range.

4.4.3   Film Breakdown Measurements

While the main focus of the study was the evaluation of variable temperature dielectric stability of polymeric materials for wide-temperature capacitor applications, high voltage (DC) dielectric breakdown measurements were performed on the metalized films after thermal cycling. High dielectric breakdown strengths are desired for capacitive energy storage because of the quadratic dependence of stored energy density on the film breakdown voltage (BDV). High voltage breakdown measurements were performed on polymer films metalized with 3 mm aluminum electrodes. A typical sample test configuration for the metalized film using high voltage power supply models Bertan 210-05 R or Spellman SR6 (with operating voltage capability up to 5 kV and 30 kV respectively) are shown in Figure 18.
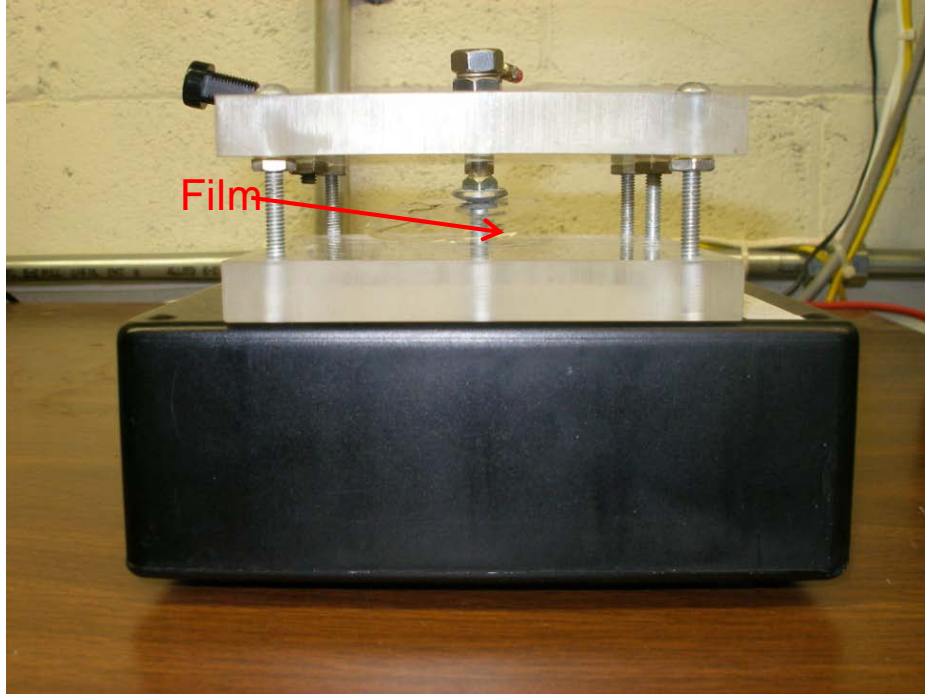
Figure 18. Test Configuration for Metalized Polymer Film with 3 mm Electrodes for Dielectric Breakdown Measurements

In all the experiments, the DC voltage was ramped at 50 volt intervals until breakdown. The resulting current was measured using a Hewlett Packard 4349A 4-Channel High Resistance Meter. The room temperature breakdown experiment was performed on metalized films already subjected to thermal cycling up to 250ºC or 350ºC for LCR measurements.

Typical room temperature electrical breakdown behavior of the metalized films is shown as current-voltage (I-V) plots and is illustrated for the PI-ADE film (Figure 19) and FDAPE film (Figure 20), already subjected to LCR measurements in the RT-250°C range and RT-350ºC range respectively. Testing of four different capacitor areas (referred to as C1, C2, C3 and C4) in the PI-ADE film reveals the highest observed BDV to be 473 V/ µm and the average BDV to be 367 V/µm for a 7.6 µm thick film. The spikes in the current, seen in some of the I-V traces, are due to 'clearing' or 'self-healing' events occurring in the capacitor device prior to complete electrical breakdown. It was observed, that in general, that the measured current at the high field breakdown threshold was of the order of a micro-ampere (µA) or higher.
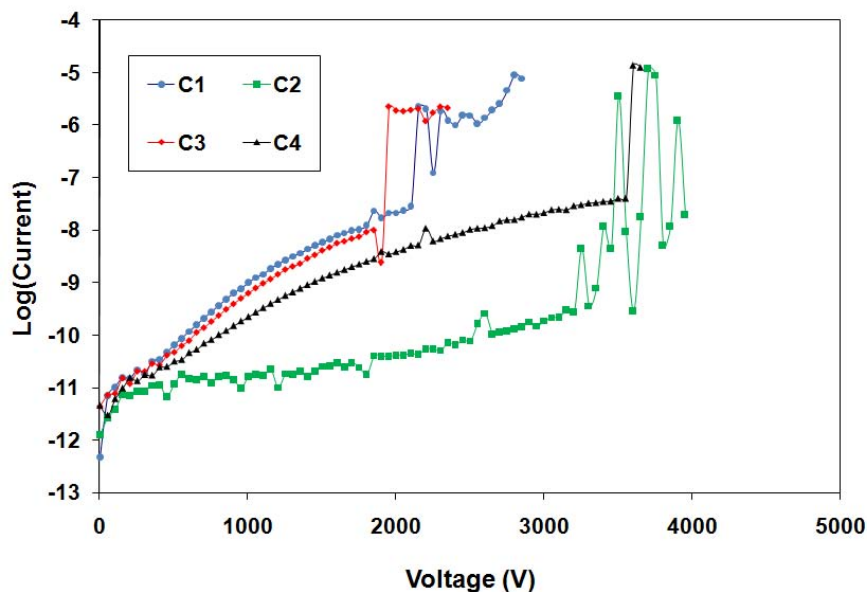
Figure 19. High Voltage Breakdown Measurement of Metalized PI-ADE film

In the case of the FDAPE film with 8 μm thickness, the measured breakdown voltage ranged from 190-275 V/μm. However, optimization of the solvent–based film fabrication process with the capability for continuous, large scale production, similar to Ferrania FPE films, can lead to much higher film breakdown strengths for FDAPE films.
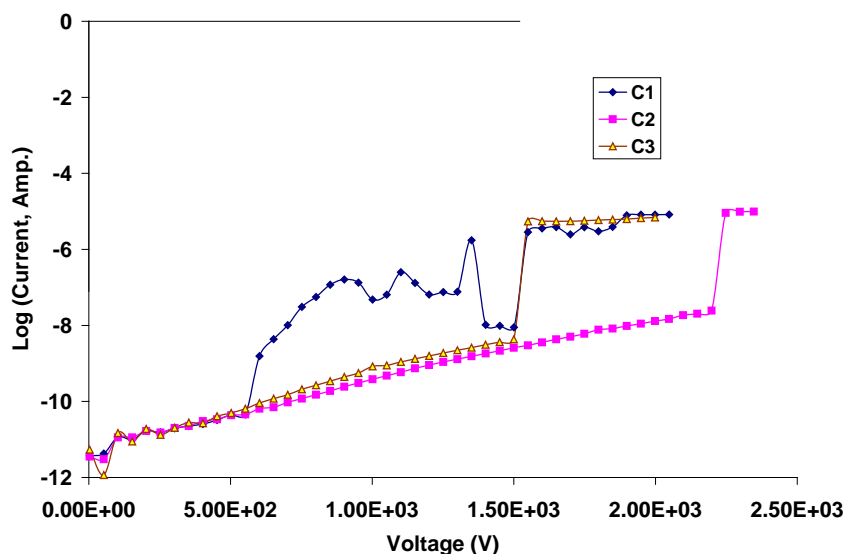
Figure 20. High Voltage Breakdown Testing of a Metalized FDAPE film

The following Table (Table 4) lists measured BDVs of various 6F-Co-PBO and FDAPE films with 3 mm Al electrodes. Reasonably good room temperature BDVs were measured for the films

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with and without the thermal history associated with cycling during LCR measurements. Based on the various films examined (Table 4), the overall average BDV ranged from 240 to 245 V/μm for 6F-Co-PBO and FDAPE. For comparison, reported room temperature BDVs for the commercial FPE (Ferrania) film is also listed. Average film breakdown strength of ~ 440 V/μm reported for the 8 μm Ferrania film can be attributed to continuous, large scale solvent casting manufacturing process under optimized conditions followed by the post-surface treatment of the film.

Table 4. Dielectric Breakdown Testing of Metalized 6F-Co-PBO and FDAPE Films

Polymer film	Film thickness (μm)	Thermal cycling history	Measured BDV (V/μm)
6F-Co-PBO	9	Up to 350ºC	282, 150
	3.5	Up to 250ºC	315
	6.5	None	250, 215
FDAPE	8	Up to 350ºC	190, 190, 275
	11	Up to 300ºC	300, 322
	9	None	205, 227
FPE (Ferrania)	50-8	--------	160-440

4.5 Comparative wide-temperature dielectric evaluation-6F-Co-PBO, FDAPE and FPE

This task was designed for the extensive dielectric investigation of metalized thin films specifically derived from 6F-Co-PBO and FDAPE films in the temperature range of RT-350ºC. The objective of the task was to compare the wide-temperature dielectric performance of 6F-Co-PBO and FDAPE films with that of a commercial FPE film under the same measurement conditions. The study focused on variable temperature dielectric measurements of film capacitance, and dissipation factor as well as insulation resistance and on the effects of thermal cycling on polymer dielectric stability. To assess the potential for long-term electro-mechanical stability of the dielectric films in power conditioning capacitors, the film thermo-mechanical and tensile (stress-strain) properties of 6F-Co-PBO, FDAPE and FPE films were extensively studied. Possible correlations between the thermo-mechanical properties of the polymer films and their high temperature dielectric properties were also examined [21].

4.5.1 Film Thermal and Thermo-oxidative Stability

Comparative thermal stability of the three polymer films is shown by the TGA traces in nitrogen in Figure 21. It was found that both FPE and FDAPE have nearly the same thermal degradation profiles (475ºC onset of degradation for FPE and 470ºC onset of degradation for FDAPE) while the onset of degradation for the 6F-Co-PBO polymer film was higher (~ 490ºC). This shows the potential for these polymer dielectrics to operate reliably in the high temperature environment of

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the power conditioning capacitors. The corresponding comparative thermal stability characteristics for the films in air are shown in Figure 22. The results are summed up in Table 5. The temperature of polymer degradation (T_d) is indicated both in terms of onset and 5 % weight loss of the film sample.
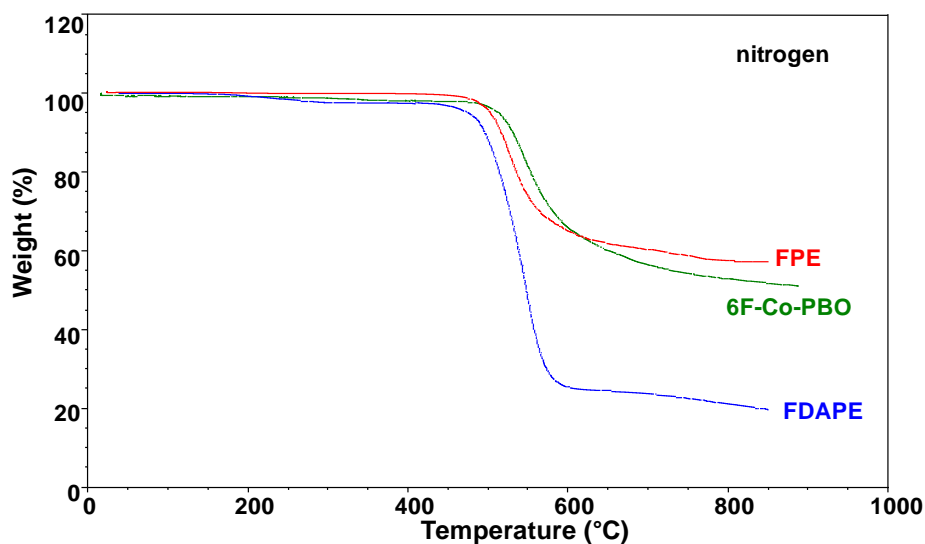
Figure 21. Comparative Thermal Stability in Nitrogen for FDAPE, 6F-Co-PBO and FPE Films
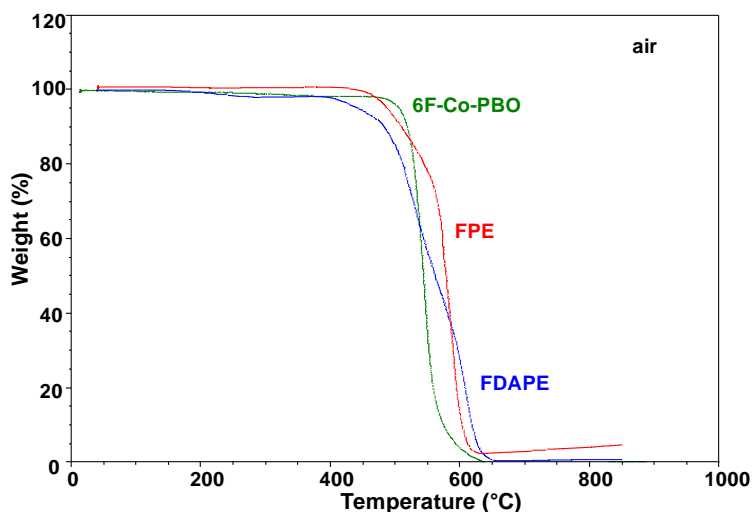
Figure 22. Comparative Thermo-oxidative Stability in Air for FDAPE,
6F-Co-PBO and FPE Films

Table 5. TGA Data for 6F-Co-PBO, FDAPE and FPE Films

Polymer film	T_d, onset, N_2, ºC	T_d, 5 wt % loss, N_2, ºC	T_d, onset, air, ºC	T_d, 5 wt % loss, air, ºC
6F-Co-PBO	490	525	475	510
FDAPE	465	490	400	465
FPE	475	500	430	490

4.5.2   Film Thermo-mechanical Properties

Thermo-mechanical profiles of the three polymer films 6F-Co-PBO, FDAPE and FPE are shown in Figure 23 as DMA plots. Since the limiting factor for the dimensional stability of the polymer dielectric is its glass transition temperature, T_gs well in excess of 350ºC are potentially required for long-term dielectric/electro-mechanical stability for the operation of the power conditioning capacitors in the vicinity of 350ºC. From the tan δ and storage modulus plots, the onset of T_g is 450ºC for FDAPE, 375ºC for 6F-Co-PBO and 330ºC for FPE, taken as the points of intersection of the storage modulus drop with the tan δ peaks. The TMA results also corroborated the high glass transition temperatures of these polymer films (Figure 24 a). While FPE and FDAPE films were found to undergo sharp, considerable dimensional changes at their T_gs, 6F-Co-PBO was found to undergo relatively less dimensional change due to stretching at its T_g. The TMA of the 6F-Co-PBO is shown on an expanded scale in Figure 24 b. The relatively small dimensional change exhibited by the 6F-Co-PBO film can be presumably attributed to the presence of the aromatic heterocyclic ring unit in the 6F-Co-PBO structure. The differences in film deformational behavior at the glass transition temperature will likely impact the long-range wide-temperature dielectric stability of these films in power system conditioning capacitors.
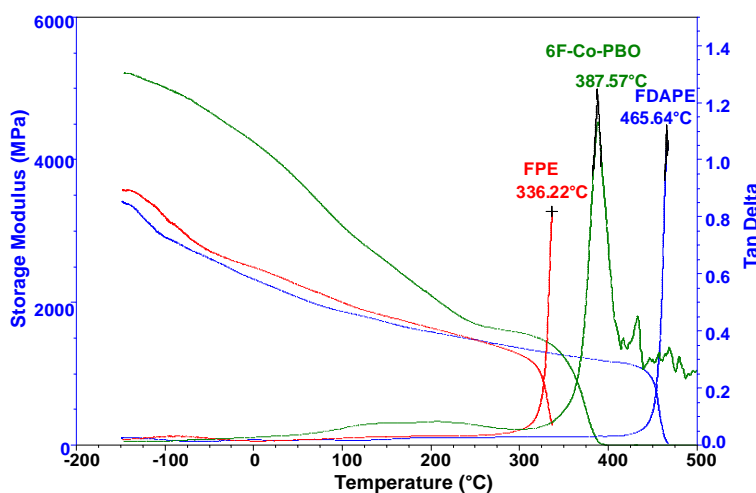
Figure 23. Thermo-mechanical Profiles by DMA for 6F-Co-PBO, FDAPE, and FPE Films
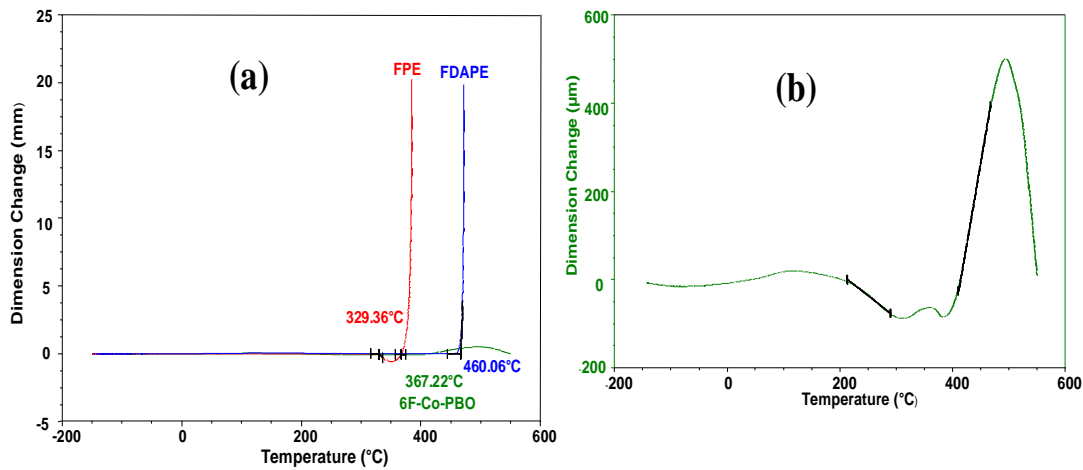
Figure 24. Thermo-mechanical Profiles by TMA for (a) 6F-Co-PBO, FDAPE, and FPE Films and (b) 6F-Co-PBO Film on Expanded Scale

4.5.3   Film Mechanical (Tensile) Properties

Typical room temperature tensile stress-strain profiles of these polymer films are shown in Figure 25. The average tensile properties of FPE and FDAPE films, listed in Table 6 (2.14-2.15 GPa tensile modulus E and 56-64 MPa tensile strength σ) are very similar. 6F-Co-PBO polymer film exhibited somewhat better mechanical properties with 2.3 GPa tensile modulus and a tensile strength of 68 MPa. The higher tensile properties of 6F-Co-PBO films can impart good mechanical integrity to thin films (5µm or less), ideally required for power conditioning capacitor applications. The average elongation-at-break ε (~14 %) was higher for 6F-Co-PBO than those for both FPE and FDAPE films (9.7 % and 8.2 % respectively, Table 6). Another interesting feature of the stress-strain plot for 6F-Co-PBO is that the film exhibited an elongation-at-yield as well at 7.5 %. This indicates that the 6F-Co-PBO film exhibits a relatively more ductile failure mode under a tensile load compared to FPE and FDAPE. Such differences in modes of film mechanical failure and factors such as yield behavior and plastic deformation could play a crucial role in influencing continuous, large scale film processing as well as the packaging of the wound capacitor device utilizing these films.
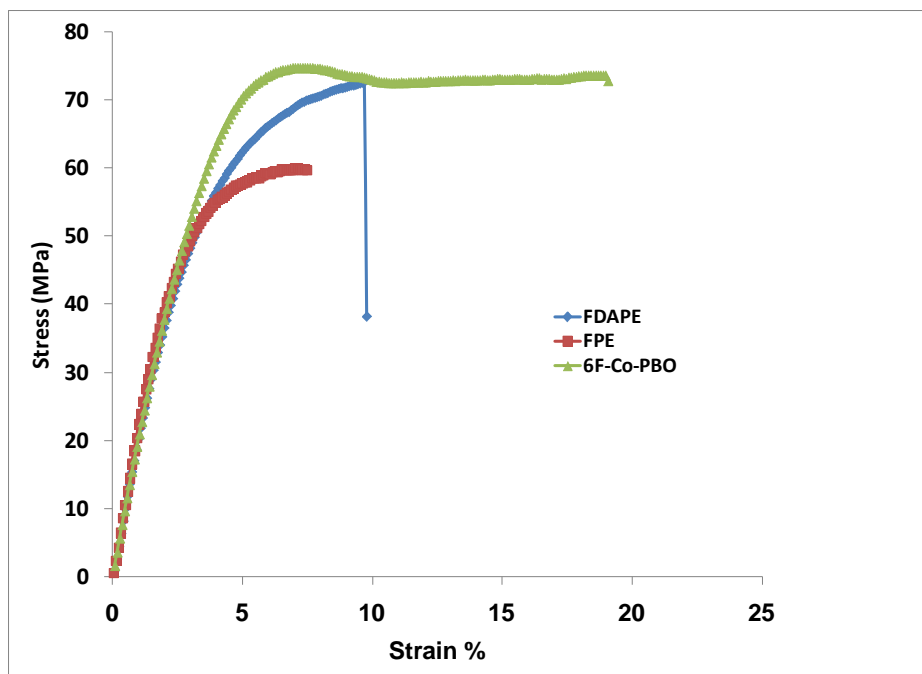
Figure 25. Room Temperature Stress-strain profiles of 6F-Co-PBO, FDAPE, and FPE Films

Table 6. Room Temperature Tensile Properties of 6F-Co-PBO, FDAPE and FPE Films

Polymer film	E (Modulus, GPa)	σ (Strength, MPa)	ε (Elongation-at-break, %)	Elongation-at-yield, %
6F-Co-PBO	2.26±0.18	67.8±8.06	14	7.5
FDAPE	2.14±0.07	63.5±7.21	8.2	----
FPE	2.15±0.29	55.9±4.01	9.7	----

4.5.4 Thin Film Fabrication of Metalized Films for Dielectric Measurements

Table 7 lists the freestanding polymer films fabricated from different solvents and their characteristics. The commercial FPE film was fabricated by Brady Worldwide Inc., from a solvent-based route.

Table 7. Solvent-based Fabrication of Freestanding Polymer Thin Films

Polymer	Solvent for film casting	Film thickness (µm)	Film quality
6F-Co-PBO	THF	3-7	Clear, ductile
FDAPE	Chloroform	5-6	Clear, ductile
FPE*	----	5-6	Clear, ductile

* Commercial film

4.5.5 Wide-temperature Film Capacitance and Dissipation Factor (DF)

To minimize errors in the evaluation of film dielectric properties especially capacitance as a function of temperature, device configurations standardized with larger area aluminum electrodes were used in the dielectric station. Besides, measurement of film capacitance over a larger effective area is a good method to assess the overall dielectric quality of a film. Examples of such device fixtures for FPE, FDAPE and 6F-Co-PBO films with film thicknesses of 5.7 µm, 5.1 µm and 3.3 µm respectively are shown in Figures 26 (a), (b) and (c). Typically, the polymer film was fully aluminized on the bottom face and 2 cm^2 circular aluminum contacts deposited through contact masks serve as the top electrodes in the measurement. Since the commercial roll of FPE film had one side fully metalized with a very thin 100 Angstroms aluminum layer, an additional 1000 Angstroms aluminum was deposited on the surface to serve as the bottom electrode.
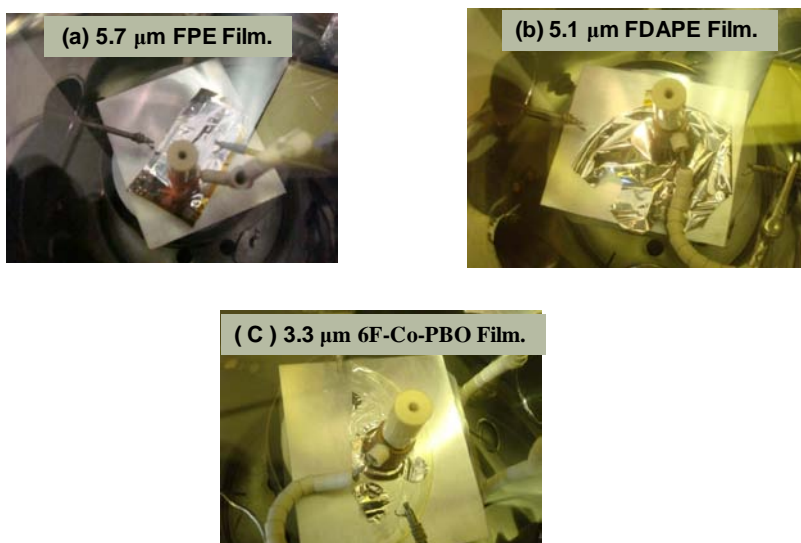
Figure 26. Test Fixtures for (a) FPE, (b) FDAPE, and (c) 6F-Co-PBO Metalized Films used in Variable Temperature LCR/IR Measurements

The measured film capacitance for the films with the 2 cm^2 testing area was typically of the order of 1-1.5 nanofarad (nF), nearly two orders of magnitude larger than the capacitance measured for films with 7 x 10^{-2} cm^2 electrode area, reported in the previous sections. The derived values of dielectric constant k at 10 kHz from the capacitance measurements were 3.4, 3.5 and 2.9 for FPE, FDAPE and 6F-Co-PBO films respectively. Variable temperature capacitance in the 100 Hz to 1 MHz frequency range from RT-350ºC (RU2 refers to 'ramp up' in the second thermal cycle) is shown for the three films in Figure 27. Overall capacitance variations in the RT-350ºC heating cycle for the three films were in the 2-3 % range. Reproducible variations were found to occur in film capacitance during the heating and the cooling cycles.
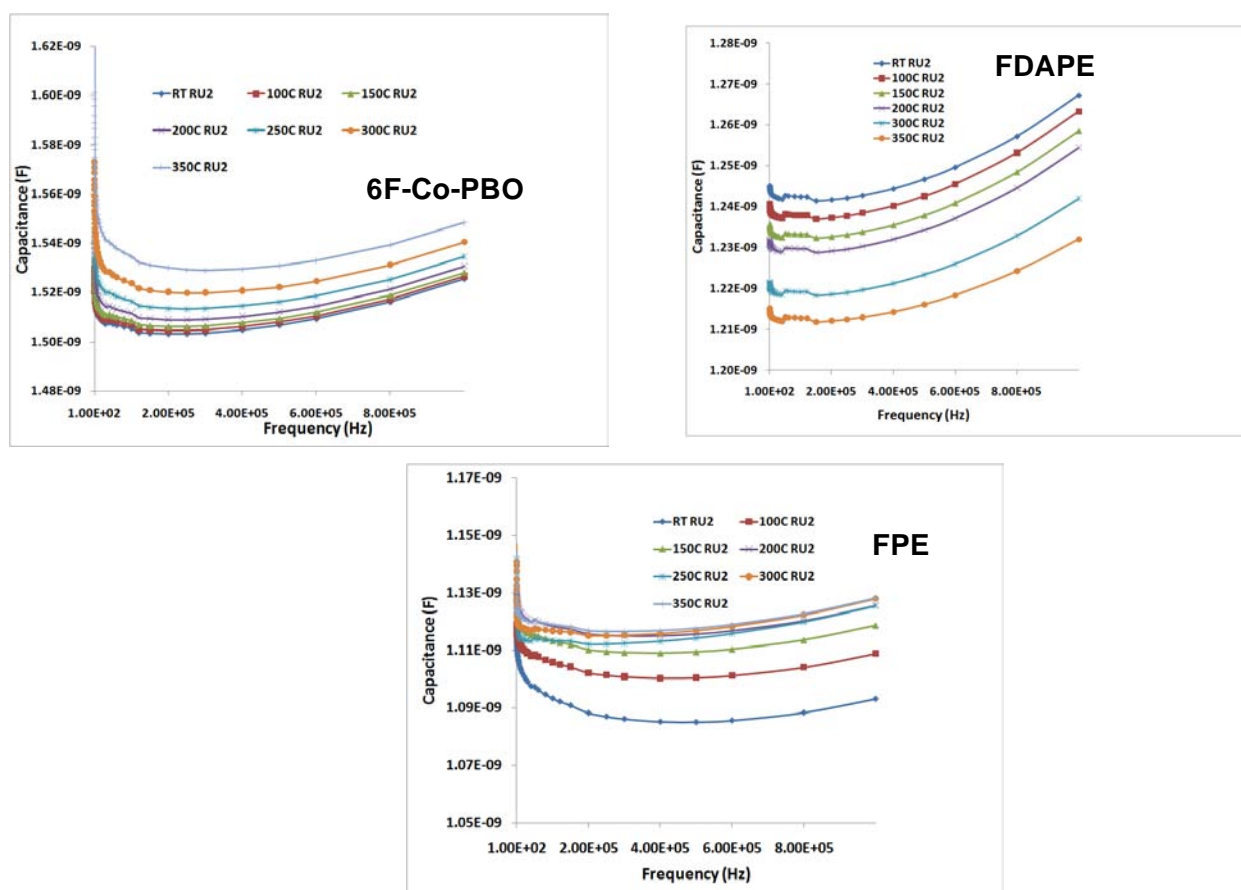
Figure 27. Variable Temperature Film Capacitance in the RT-350ºC Range
for 6F-Co-PBO, FDAPE, and FPE Films

While a small, steady enhancement was found for film capacitance as a function of temperature in the case of both 6F-Co-PBO and FPE films, a slight decrease in the temperature-dependent capacitance was found to occur in the case of FDAPE films in the RT-350ºC range. To assess the relative wide-temperature dielectric stability of the films, % Capacitance change (TCC) and dissipation factor DF (%) as a function of temperature are shown in Figures 28 and 29

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respectively. The variable temperature profiles shown in these Figures are based on measurements at 10 kHz frequency during the second heating cycle. In general, no variability in the data was observed relative to the measured values in the first heating cycle. FPE and FDAPE films were found to undergo minimal changes in TCC as a function of temperature (2.0 % and -2.4 % respectively) while a marginally higher TCC (3.0 %) was observed in the case of the 6F-Co-PBO film in the RT-350ºC range (Figure 28).
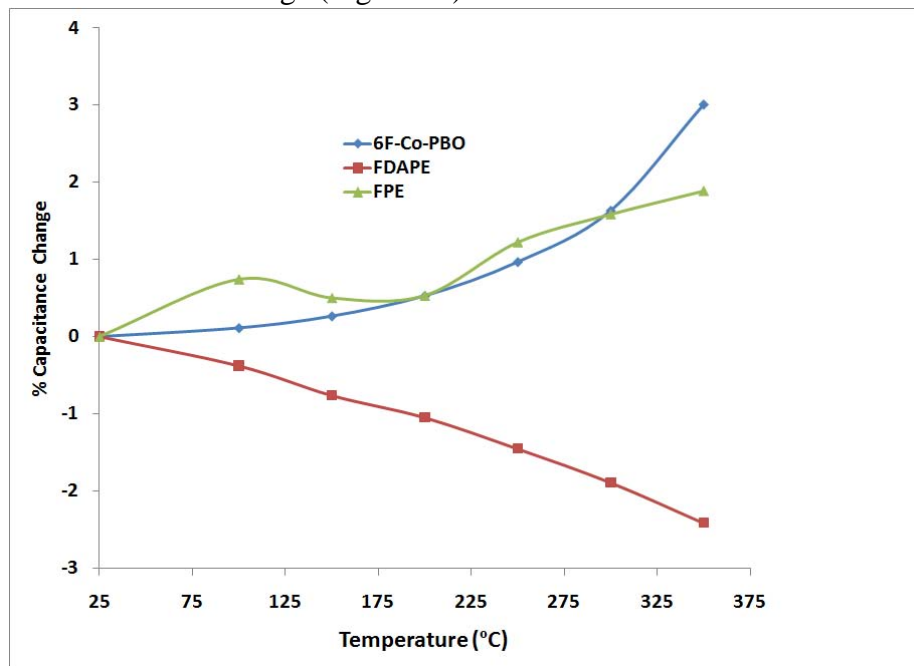
Figure 28. Capacitance Variation vs. Temperature at 10 kHz for the Polymer Film Dielectrics
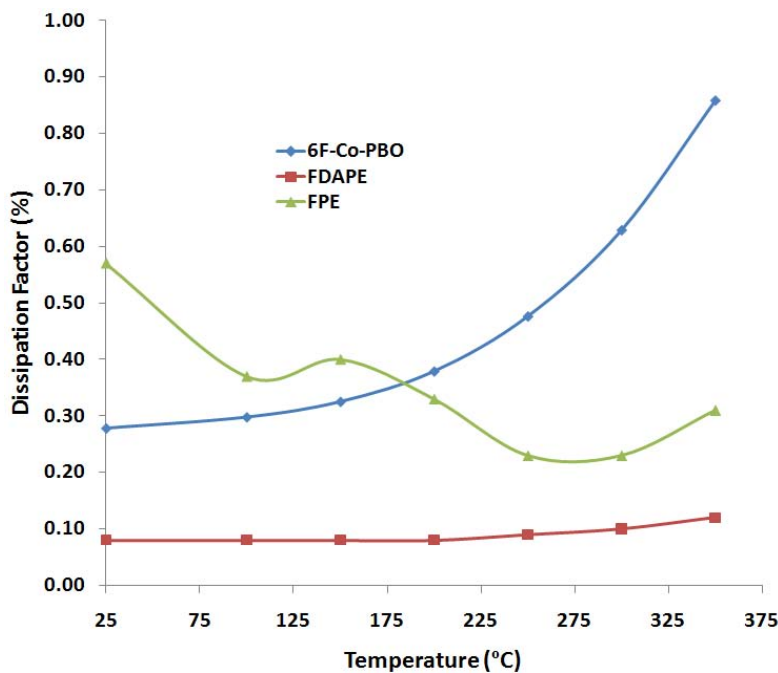
Figure 29. Film Dissipation Factor (%) as a Function of Temperature at 10 kHz
for the Polymer Film Dielectrics

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However, at temperatures in the 300-350°C range, relatively sharper variations in measured film capacitance were observed for 6F-Co-PBO. An analysis of the DF-temperature profiles of the three polymers (Figure 29) reveals the following. FDAPE film showed the lowest variable temperature DF among the films tested, with the DF slightly increasing from 0.08 % at RT to 0.12 % at 350°C. In the case of FPE, the DF was found to fluctuate in the 0.3 %-0.6 % range. For the 6F-Co-PBO film, DF was found to increase threefold from 0.3 % at RT to 0.9 % at 350°C. Again, pronounced increase in DF values at 300°C and above was clearly discernible in the case of the 6F-Co-PBO film. In the case of 6F-Co-PBO, the increase in variable temperature film capacitance is found to cause a concomitant increase in DF, seemingly in accordance with $DF = \omega.C.ESR.$ However, in the case of FDAPE film, there is a slight increase in DF as a function of temperature though the capacitance decreases by >2 % over the entire temperature range. The DF increase can then be ascribed to a possible increase in film leakage current at high temperatures.

Since FPE has a rated stability for utilization only up to a tested temperature of 200°C due to issues with packaging, it was somewhat surprising that we observed a low TCC for the FPE film tested up to even 350°C. Presumably, short-term excursions into thermal environments somewhat exceeding the glass transition temperature (330°C) of FPE did not result in significant dimensional changes that would affect its wide-temperature dielectric stability in the RT-350°C range. Its dielectric stability was comparable to that of FDAPE film at 350°C which was clearly much lower than the T_g of FDAPE (~ 450°C). However, comparative assessment of long-term reliability of these films would require thermal aging studies and investigation of dielectric stability in an even wider temperature range (up to or exceeding 400°C). It will be interesting to examine the FPE film at temperatures well above its T_g, in order to observe the effect of enhanced polymer segmental mobility on its dielectric behavior.

The significant enhancement in DF (%) values and the relatively sharp variations in % capacitance increase at the higher temperatures of 300°C and 350°C for 6F-Co-PBO can be tentatively ascribed to an increase in the polarizability of the polymer dielectric. A plausible explanation is based on the thermally-induced changes in the intra-chain hydrogen bonding involving the hydroxyl group and the benzoxazole heterocycle in 6F-Co-PBO (Figure 30); this can potentially enhance both dissipation factor and dielectric permittivity due to a change in the polarization of the hydroxyl side groups attached to the polymer backbone. Presumably, since 6F-Co-PBO film is still in the glassy state (T_g~375°C) at the operational temperatures of 300°C and 350°C, dimensional changes occurring in the metalized polymer dielectric may be too insignificant to cause any sharp variations in film dielectric behavior at these temperatures. In addition, TMA of the 6F-co-PBO film (Figure 24) has shown that the 6F-Co-PBO film undergoes a relatively small dimensional change at its T_g.
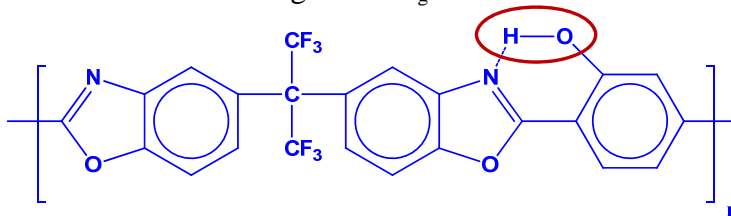
Figure 30. Intra-molecular Hydrogen Bonded Structure of the 6F-PBO unit
with the Hydroxyl Group

High frequency power converters require stable capacitor operation at ≥ 100 kHz frequencies. The film dissipation factor as a function of three different frequencies (1, 10 and 100 kHz) over the RT-350ºC range is also shown to examine the potential of these films for high frequency operation (Figures 31-33 respectively for FDAPE, FPE and 6F-Co-PBO films).
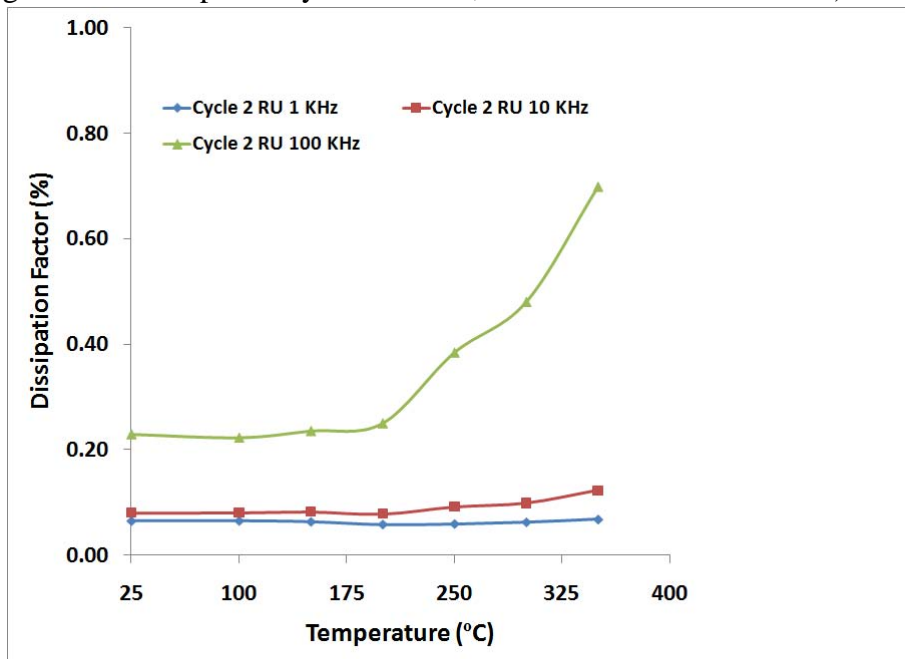
Figure 31. DF vs. T Measured at Different Frequencies for FDAPE Film
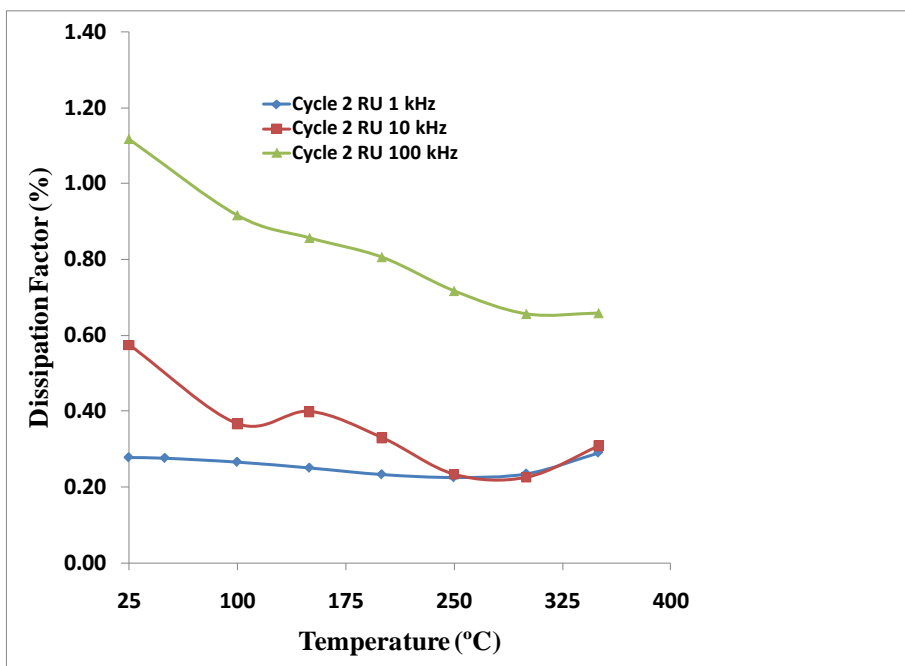
Figure 32. DF vs. T Measured at Different Frequencies for FPE Film

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FDPE film exhibited very low, variable temperature DF at both 1 kHz and 10 kHz frequencies. DF was found to increase sharply at and above 250ºC at 100 kHz frequency but was still < 1 % at 350ºC (Figure 31). FPE film also showed (Figure 32) increasingly higher DF with increase in frequency over the entire temperature region. At all frequencies, DF was found to decrease with temperature up to 250ºC or 300ºC but then gradually rose at higher temperatures. In the case of both FDAPE and FPE films, the measured DF at 100 kHz was ~ 0.7 %.

The DF profile for 6F-Co-PBO film over the RT-350ºC range as a function of frequency is shown in Figure 33. While there was a steady increase in the measured DF as a function of temperature at the three frequencies, the film showed a decreasing trend for DF with increasing frequency from 1 kHz to 100 kHz. Analysis of the DF data in Figures 31-33 seems to indicate that all the films exhibit an acceptably low DF (0.65-0.70 %) at 100 kHz and 350ºC.
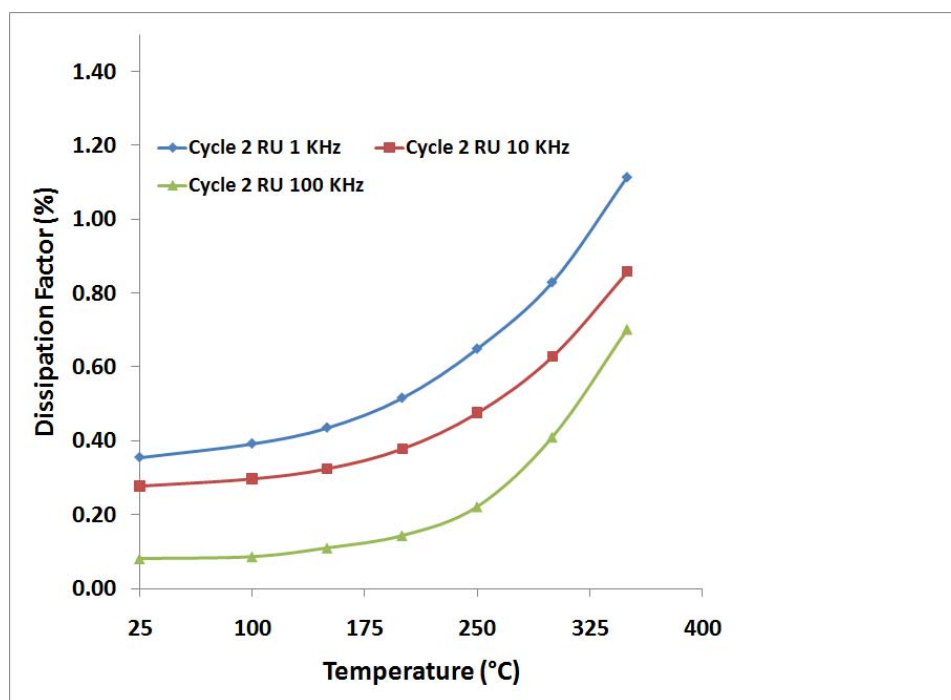
Figure 33. DF vs. T Measured at Different Frequencies for 6F-Co-PBO Film

4.5.6   Wide-temperature Comparative Film Insulation Resistance Data

Variable temperature insulation resistance data up to 350ºC, with 40V DC as the test voltage for 6F-Co-PBO, FDAPE and FPE films are shown in Figure 34.
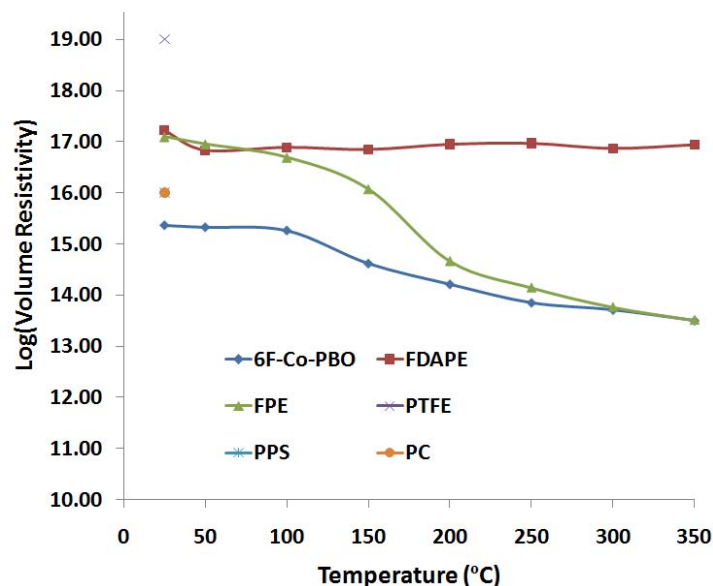
Figure 34. Comparison of Variable Temperature IR of the Films (also shown: RT Resistivity of some Common Commercial Polymer Films)

The measured values of room temperature volume resistivity of FPE and FDAPE were very similar, 1.2 x 10^{17} and 1.7 x 10^{17} ohm.cm respectively. In the case of 6F-Co-PBO, the room temperature resistivity was somewhat lower (2.7 x 10^{15} ohm.cm). For comparison, the reported room temperature resistivity values of some commercial polymer films evaluated for capacitor applications are also shown. PTFE shows the highest resistivity (10^{19} ohm.cm) while PC and PPS films show RT resistivity of 10^{16} ohm.cm.

Interesting variations in wide-temperature IR characteristics were observed for the different polymer films in the RT-350ºC range. In the case of FPE, there was an overall decrease in volume resistivity by nearly four orders of magnitude from 1.2 x 10^{17} ohm.cm at RT to 3.2 x 10^{13} ohm.cm at 350ºC. This may be partially due to the presence of proprietary filler incorporated during the processing of the FPE film in order to lower the coefficient of friction ("stickiness") of the thin film [22]. The corresponding resistivity decrease for the 6F-Co-PBO film was from 2.7 x 10^{15} to 3 x 10^{13} ohm.cm and FDAPE exhibited considerably less variation in volume resistivity, with a decrease from 1.7 x 10^{17} to 8.7 x 10^{16} ohm.cm in the entire RT-350ºC range. The high temperature insulation resistance of FDAPE was the highest among the three polymer films tested.

4.5.7 Wide-temperature LCR Measurements up to 400ºC.

Wide-temperature film LCR measurements were also extended to 400ºC as the upper limit for 6F-Co-PBO, FDAPE and FPE films. The objective was to provide further comparison between the three high temperature films in terms of their short-term variable temperature dielectric behavior. While in the case of the FDAPE film, the measurement temperature of 400ºC was below its T_g of 450ºC, it was be slightly above the of T_g (375ºC) of the 6F-Co-PBO film and substantially higher than that (330ºC) of the FPE film.

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The 6F-Co-PBO film capacitance, % capacitance change and dissipation factor, measured up to 400ºC are shown in Figures 35 a, 35 b and 36 respectively. The thermal history of this film included two complete thermal cycles in the RT-350ºC range for LCR measurements. The plots shown here are based on LCR data specifically focusing on the high temperature region between 200-400ºC.
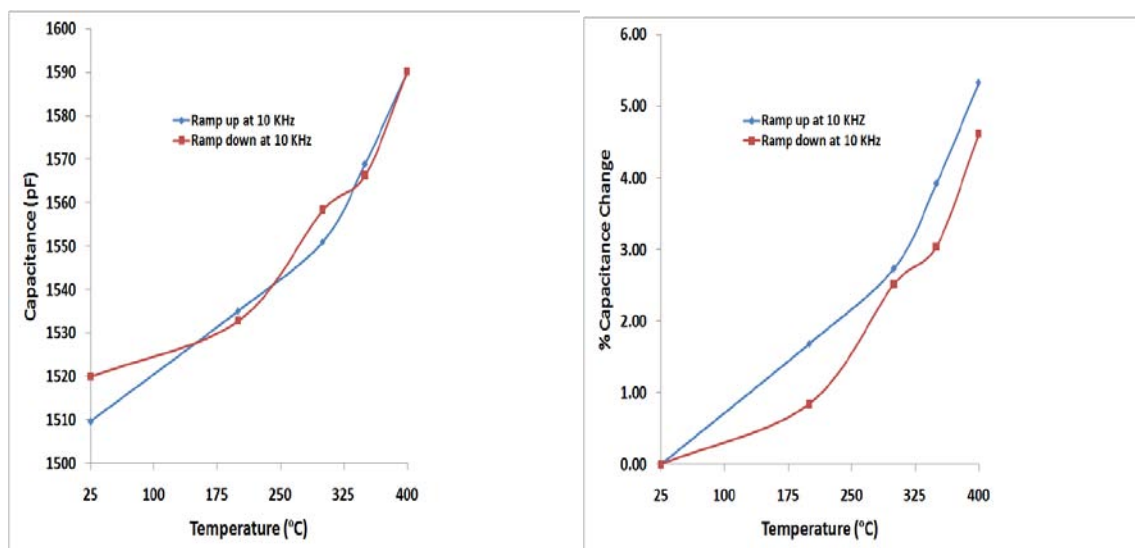
Figure 35. RT-400°C Measurements (a) Capacitance and (b) % Capacitance Change at 10 kHz Frequency for 6F-Co-PBO Film
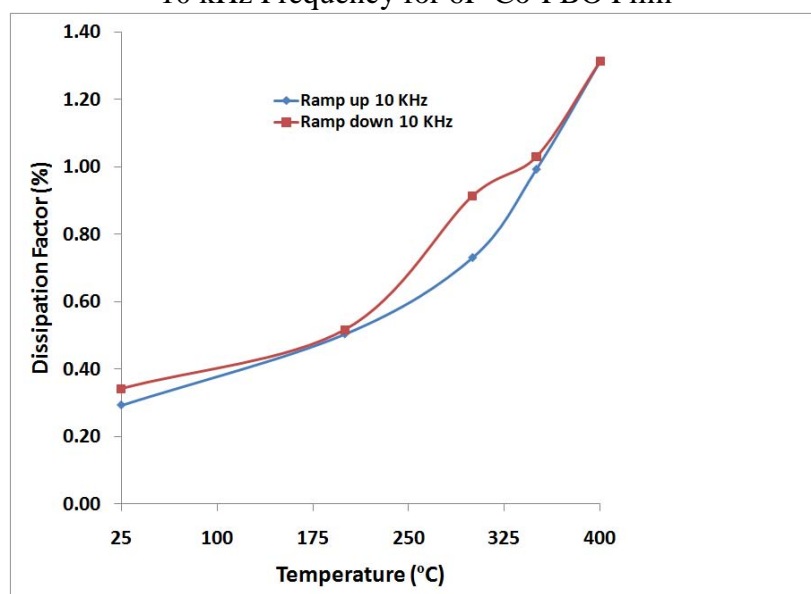
Figure 36. DF (%) Measured at 10 kHz Frequency in the RT-400ºC Region for 6F-Co-PBO Film

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Larger TCC (~ 5.3 % corresponding to an increase in capacitance from 1510 to 1590 pF) was noted in the RT-400ºC region for the 6F-Co-PBO film relative to what was measured in the RT-350ºC thermal cycle (Figure 28). Likewise, a further increase in film DF to 1.3 % was observed for the 6F-Co-PBO film at 400ºC relative to the DF measured at 350ºC (0.9 %) in the RT-350ºC thermal cycle (Figure 29). However, reversibility of dielectric behavior in terms of both % capacitance change as well as DF during the cooling cycle confirms wide-temperature dielectric stability, at least for the short-term in the RT-400ºC range.

The corresponding wide-temperature dielectric measurements in the RT-400ºC range for the FDAPE film, already subjected to a RT-350ºC thermal cycle for IR measurements, are shown in Figures 37 and 38.
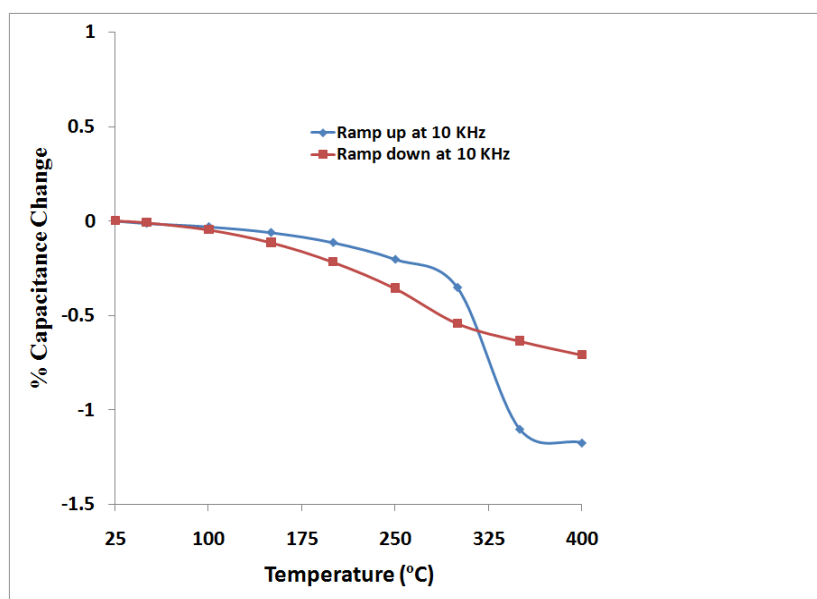
Figure 37. Capacitance Change (%) Measured at 10 kHz Frequency in the
RT-400ºC Region for FDAPE Film

The measured TCC was ~ -1.25 % during the ramp up to 400ºC and < 1 % during the ramp down from 400ºC. There were virtually no differences in the FDAPE wide-temperature dielectric behavior relative to what was observed for the RT-350ºC thermal cycling experiment (Figure 28). Figure 38 depicts the DF, at 10 kHz frequency, of the film as a function of temperature.

41
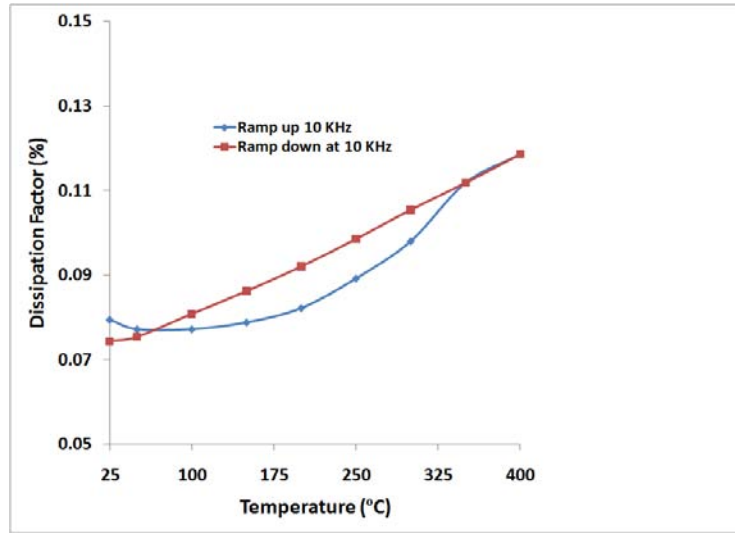
Figure 38. DF (%) Measured at 10 kHz Frequency in the
RT-400ºC Region for FDAPE Film

Film DF was found to increase from 0.07 to 0.12 % in the entire RT-400ºC region, demonstrating remarkably low values. This trend is indistinguishable from the variable temperature film behavior in the RT-350ºC range shown in Figure 29. Variable temperature film LCR measurements were also performed in RT-400ºC range for the FPE film. TCC and DF as a function of temperature at 10 kHz frequency are shown in Figures 39 and 40 respectively.
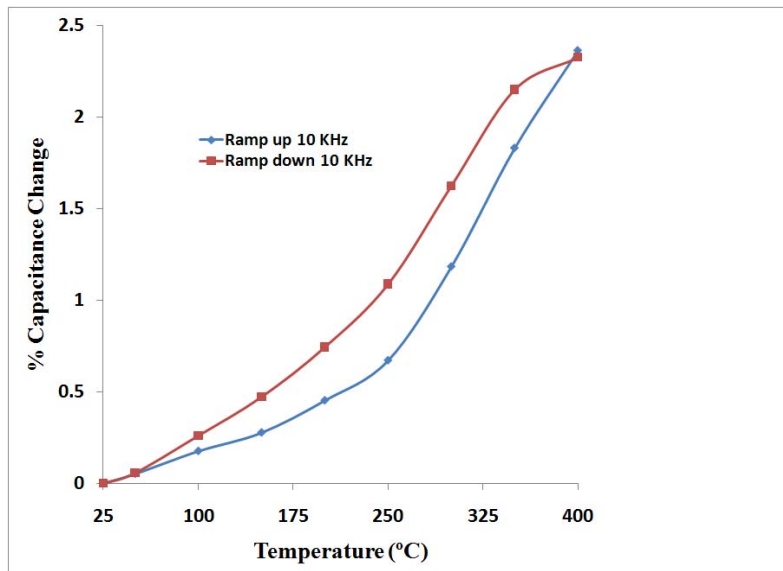
Figure 39. Capacitance Change (%) Measured at 10 kHz Frequency in the
RT-400ºC Region for FPE Film
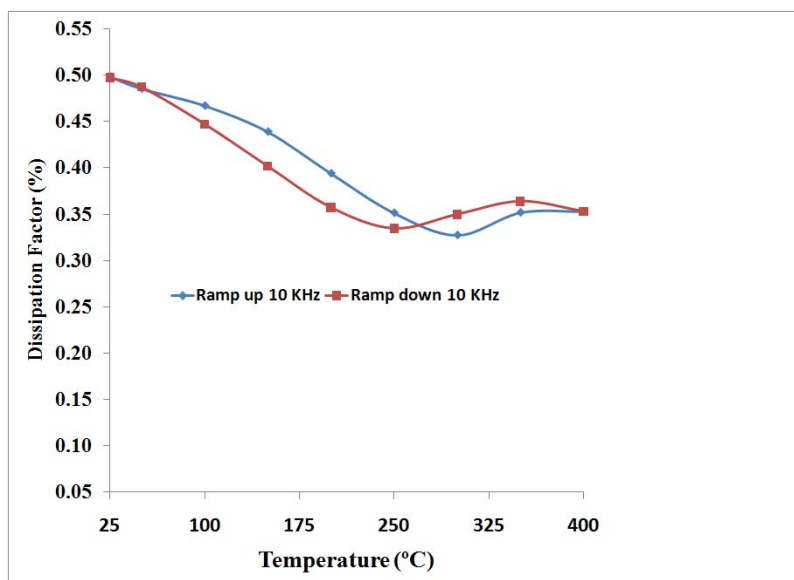
Figure 40. DF (%) Measured at 10 kHz Frequency in the RT-400ºC Region for FPE Film

Relatively higher TCC and DF were observed at 400ºC for the FPE film (Figures 39 and 40) compared to the observed values at 350ºC (Figures 28 and 29). However, the enhancements were not significant and the cyclability of the dielectric data during heating and cooling indicates short-term electro-mechanical stability for the FPE film even at the higher temperature environment of 400ºC.

4.5.8   Film LCR Measurements with Applied DC Bias

Variable temperature film LCR measurements in the RT-350ºC were also conducted for FPE and 6F-Co-PBO films with 1V oscillating voltage and 10V-40V applied DC bias. The software was set up for performing a number of LCR scans with varying DC bias voltage levels at a given temperature. TCC and DF (%) as a function of temperature in the RT-350ºC range under a DC voltage stress of 10-40 V are shown in Figures 41 and 42 respectively for the 5.7 µ thick FPE film.
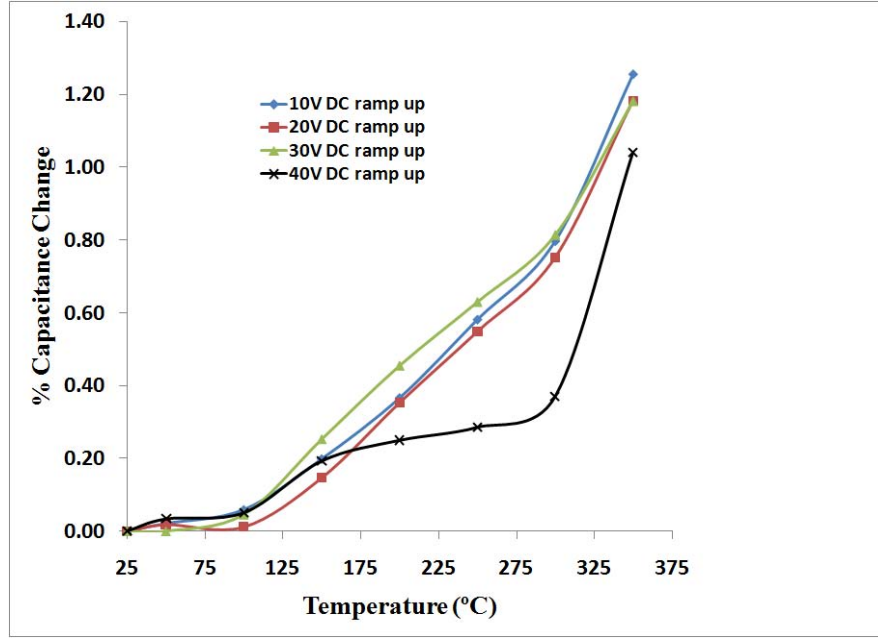
Figure 41. Capacitance Change (%) for FPE Film in the RT-350ºC Range Measured at 10 kHz Frequency and with the Application of DC Voltage Bias
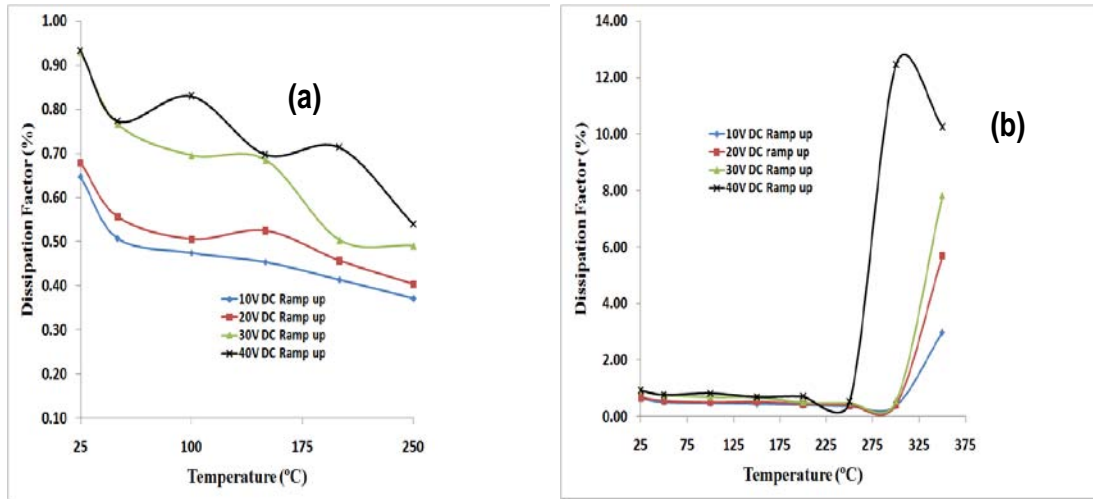
Figure 42. Variable Temperature DF (%) for FPE Film Measured at 10 kHz Frequency and with the Application of DC Voltage Bias: (a) up to 250ºC (b) up to 350ºC

DC bias in the 10-40V range does not seem to have a significant influence on TCC. DF was found to increase steadily with applied DC bias in the entire temperature range. While the overall increase in DF as a function of DC bias was gradual up to 250ºC, it was found to be markedly affected by higher applied DC voltage at temperatures ≥ 300ºC. This is evidenced by a steep increase in DF (> 12 % at 300ºC/40 V DC bias, more than an order of magnitude higher than the

DF at 250ºC and 40V DC applied voltage stress). The increase in DF may be caused by a field-sensitive dielectric relaxation effect close to the film T_g of 330ºC for the FPE film.

The corresponding variable temperature LCR measurement results for a 6.5 μ 6F-Co-PBO film are shown in Figures 43 and 44. Variable temperature TCC as well as DF, measured at 10 kHz in the RT-350ºC range with varying applied DC bias voltage levels (0-40 V) are depicted for both heating and cooling cycles.
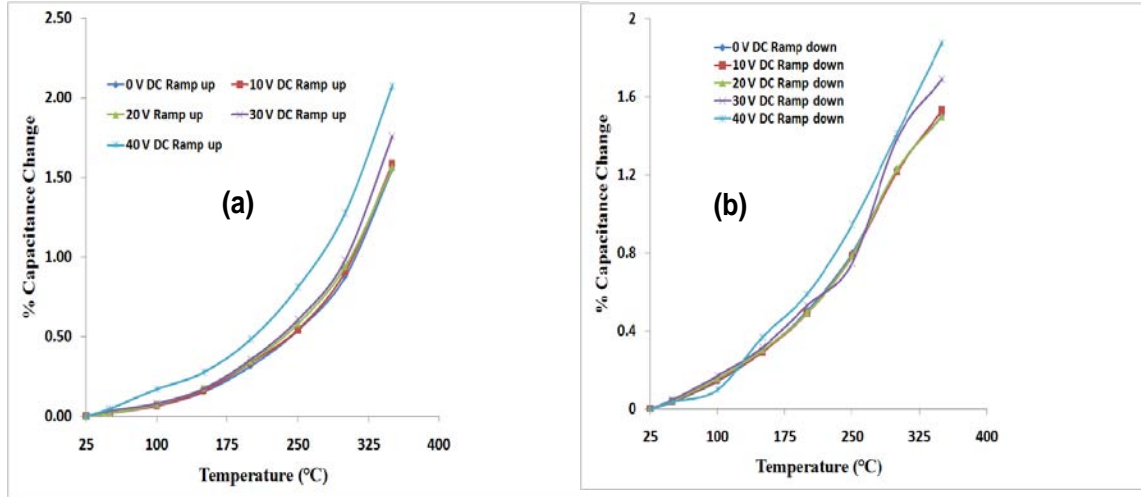
Figure 43. Capacitance Change (%) for 6F-Co-PBO Film in the RT-350ºC Range Measured at 10 kHz frequency and with the Application of DC Voltage Bias (0 V-40 V) (a) during Heating and (b) during Cooling
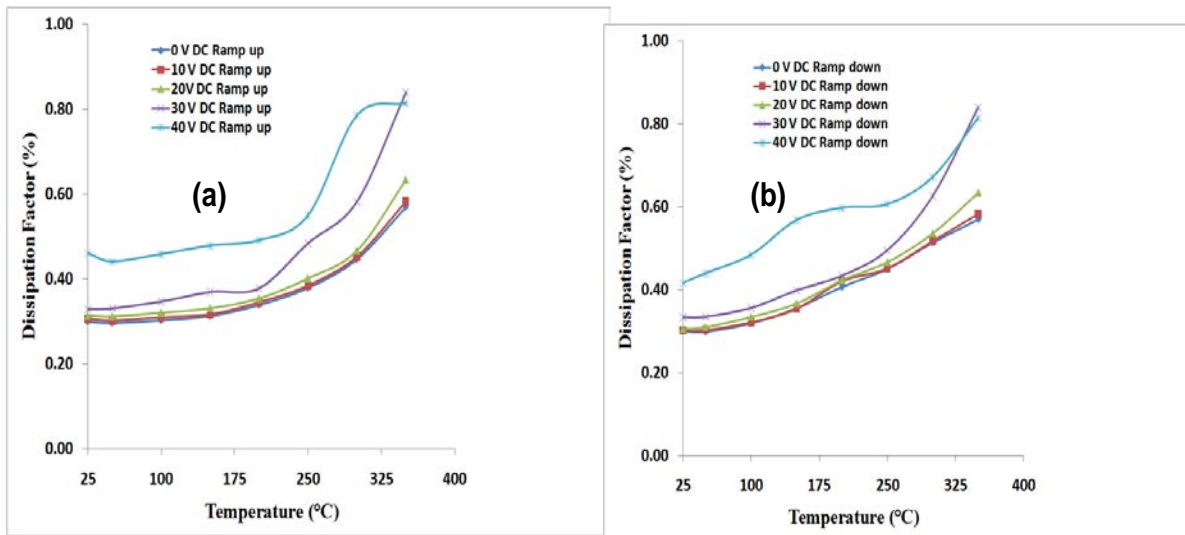
Figure 44. Variable Temperature DF (%) for 6F-Co-PBO Film in the RT-350ºC Range Measured at 10 kHz Frequency and with the Application of DC Voltage Bias (0 V-40 V) (a) during Heating and (b) during Cooling

Both capacitance change and DF increased with both temperature and applied DC bias voltage. Significant increase in film DF was found to occur at temperatures exceeding 250ºC and at applied DC bias of 30 V and 40 V. However, the measured DF was < 1 % even at 350ºC and at 40 V DC bias. Clearly, from the DF results, it can be discerned that the 6F-Co-PBO film exhibits much better wide-temperature dielectric stability as a function of applied DC voltage stress than the FPE film evaluated under the same conditions.

4.6   FPE film dielectric breakdown measurements

The dielectric breakdown voltage of the Ferrania FPE films has been reported to be in the range of 160 V/μm-440 V/μm for film thickness in the range of 50-8 μm (Table 4).

The RT dielectric breakdown of the FPE film (6.2 μm thick, with 3 mm top and bottom Al electrodes), already subjected to thermal cycling in the RT-350ºC range, was measured in this study.   The I-V plots are shown in Figure 45.
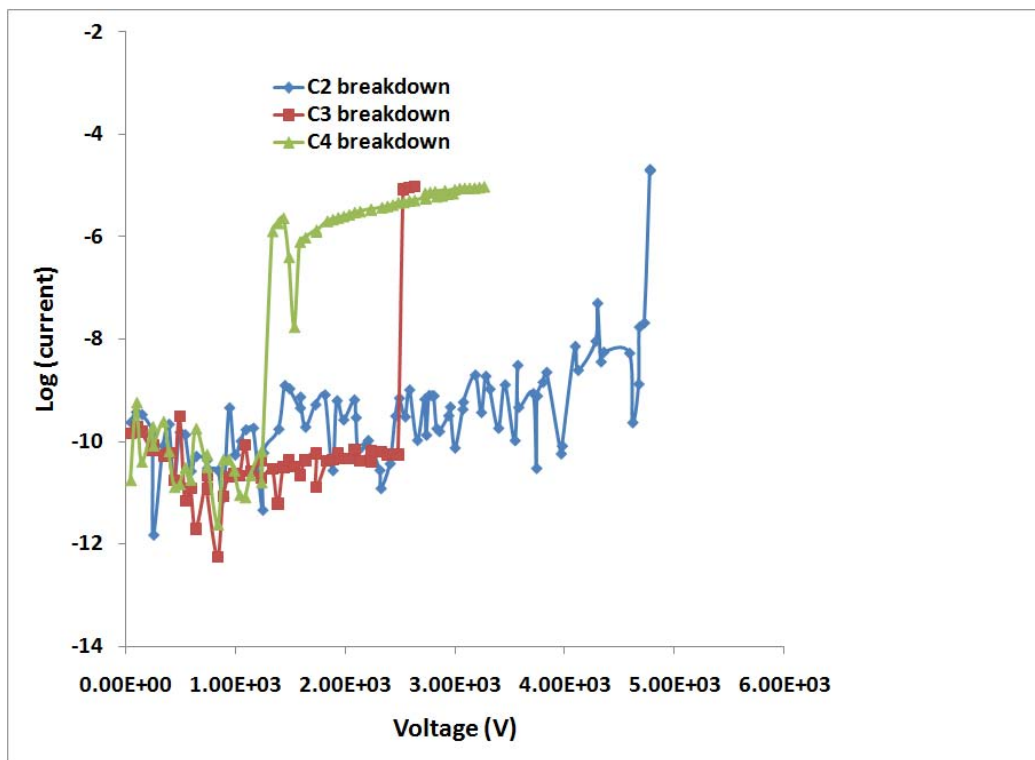
Figure 45. High Voltage Breakdown Testing of a Metalized Freestanding FPE Film

The measured film breakdown strength based on three different capacitor areas had wide variability with BDV of 214 V/μm, 408 V/μm and 702 V/μm. The average BDV was 441 V/μm. The occurrence of several 'clearing' or 'self-healing' events (surges of current) prior to breakdown is indicated in the plots.

An alternative protocol was also employed to measure the BDV of the unmetalized FPE film (Figure 46). This breakdown methodology utilizes biaxially oriented Polypropylene (BOPP) films, metalized on one face, as electrodes [23, 24]. The unmetalized dielectric film FPE was placed over the metalized face of BOPP serving as the bottom electrode. Metalized BOPP with the aluminum face down served as the top electrode. To define the active area for the breakdown measurement, a Kapton mask with a 2 cm^2 window was placed between the top electrode and the film being tested. A small area of the aluminum face of the top electrode was rolled up to expose the metal layer for making electrical connection.
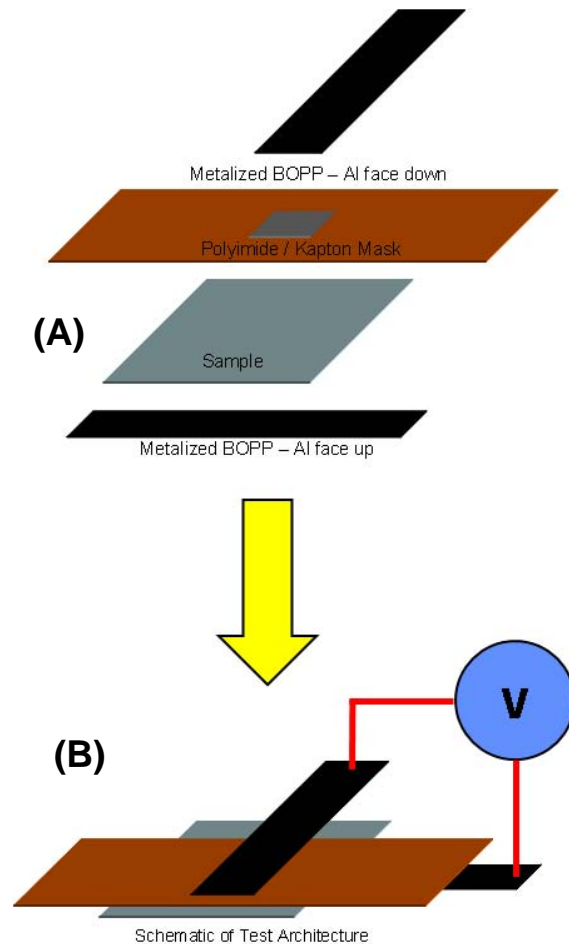
Figure 46. Schematic of the Dielectric Breakdown Strength Measurement Set-up (a) the Various Layers shown Separated and (b) during Breakdown Voltage (BDV) Measurement

When a ramp DC voltage was applied, the layers were drawn together by electrostatic force. Typically, 300-500 V potential was required to establish intimate contact within the device via electrostatic attraction. Figure 47 shows the high voltage breakdown behavior of the FPE film using this method.
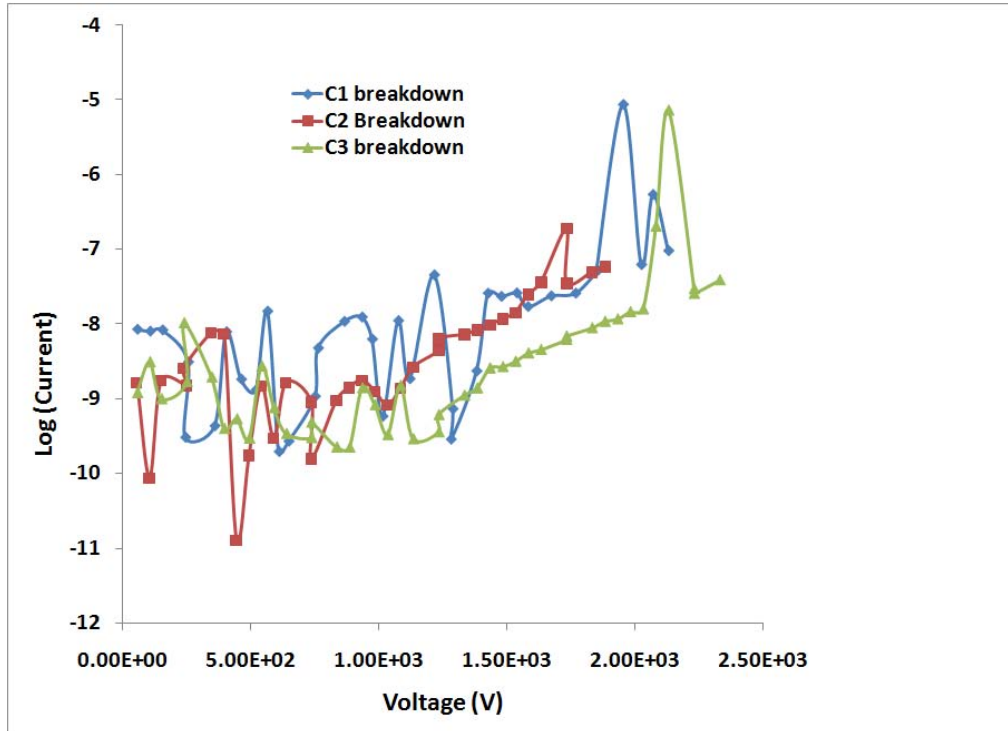
Figure 47. Dielectric Breakdown of FPE Film using Metalized BOPP as Electrodes

Based on three breakdown voltage measurements of 343 V/μ, 316 V/μ and 280 V/μ, the average BDV was 313 V/μ. The measured values of breakdown by this method were fairly close to each other.

5.0 Conclusions

Some of the DoD requirements for wide-temperature Air Force power electronic applications have been addressed via the in-house design, development and dielectric investigations of several high temperature polymer films. The design criteria were geared towards enhancing the reliability of the power system by efficiently decreasing the thermal load for electronic system cooling. Towards meeting the objective of dielectric/electro-mechanical stability for wide-temperature power electronics applications, thermally robust thin polymer films with high glass transition temperatures (T_gs, 305-450ºC) as well as high thermal stabilities (470-520ºC) were evaluated for power conditioning capacitor applications at temperatures ≥ 300ºC. The initial screening studies included a relatively broad spectrum of polymeric materials based on a fluorinated polyimide with an adamantyl ester pendant (PI-ADE), a fluorinated polybenzoxazole copolymer with a hydroxyl pendant (6F-Co-PBO) and a fluorenyl polyester with a diamantyl structural unit (FDAPE). Initial studies clearly point to the dielectric stability of these films for high temperature power conditioning applications, as indicated by their relatively low temperature coefficient of capacitance (TCC) (~ 2 %) up to 250-350ºC range as the upper temperature limits.

The second phase of the dielectric investigations specifically focused on the extensive variable temperature evaluation of metalized thin films of 6F-Co-PBO (T_g =375ºC) and FDAPE (T_g = 450ºC) in the RT-350ºC range; a comparative evaluation of the state-of-the-art fluorenyl polyester film FPE, with a T_g of 330ºC, was also performed. The capacitance of the metalized thin films measured over a 2 cm^2 area was typically in the range of 1.0-1.5 nF. The temperature coefficient of capacitance ranged from 2-3.5 % in the RT-350ºC range for the three films, FPE, FDAPE and 6F-Co-PBO. An analysis of the dissipation factor DF-temperature profiles of the three polymers revealed the following. FDAPE film showed the lowest DF among the films tested, with the DF increase from 0.08 % at RT to 0.12 % at 350°C. In the case of FPE, the DF was found to fluctuate in the 0.3 %-0.6 % range. For the 6F-Co-PBO film, DF was found to increase threefold from 0.3 % at RT to 0.9 % at 350°C.

The significant enhancement in DF (%) values and the relatively sharp increase in % capacitance change at the higher temperatures of 300°C and 350°C for the 6F-Co-PBO film can be tentatively ascribed to a change in the polarizability of the polymer dielectric. A plausible explanation is based on the thermally-induced changes in the intra-chain hydrogen bonding involving the hydroxyl pendant and the heterocycle in 6F-Co-PBO at these high temperatures; this can potentially enhance both dissipation factor and dielectric permittivity due to a change in the polarization of the hydroxyl side groups attached to the polymer backbone. Since FPE has a rated stability for utilization up to 200°C, it was somewhat surprising that we observed a low TCC for the FPE film tested even up to 350°C. Presumably, short-term excursions into thermal environments somewhat exceeding the glass transition temperature (330°C) of FPE did not seem to affect its wide-temperature dielectric stability in the RT-350°C range. Its short-term dielectric stability was comparable to that of FDAPE film at 350°C which was clearly much lower than the T_g of FDAPE (~ 450°C).

Interesting variations in wide-temperature insulation resistance characteristics were also observed for the different polymer films in the RT-350ºC range. In the case of FPE, there was an overall decrease in volume resistivity by nearly four orders of magnitude from 1.2×10^{17} ohm.cm at RT to 3.2×10^{13} ohm.cm at 350ºC. 6F-Co-PBO showed resistivity decrease from 2.7×10^{15} to 3×10^{13} ohm.cm and FDAPE exhibited considerably less variation in volume resistivity, with a decrease from 1.7×10^{17} to 8.7×10^{16} ohm.cm in the entire RT-350ºC range. The high temperature insulation resistance of FDAPE was the highest among the three polymer films examined.

In the second phase of the film dielectric studies, wide-temperature film LCR measurements were also extended to 400ºC as the upper operating temperature for 6F-Co-PBO, FDAPE and FPE films. Measured TCC and DF (%) in the RT-400ºC range for the three films indicated the following. Somewhat larger TCC (up to 5.3 % for 6F-Co-PBO and 2.5 % for FPE) and DF were observed for both 6F-Co-PBO and FPE at 400ºC relative to the measured values for the films in the RT-350ºC range. In the case of the FDAPE film, the low TCC and DF observed in the RT-400ºC range were indistinguishable from the measured values in the RT-350ºC range. TCC and DF were also examined in the case of both 6F-Co-PBO and FPE films in the RT-350ºC range with the application of 1V oscillating voltage and 10V-40V DC bias. In general, DC bias did not seem to have a significant influence on TCC in the RT-350ºC range but significant changes in DF were found to occur at temperatures at $\geq$ 300ºC for both films at the higher applied DC stress levels of 30 V and 40 V. However, the measured DF was still < 1 % for 6F-Co-PBO at 350ºC and 40 V DC bias. However, in the case of FPE, a steep increase in film DF (> 12 %) was noted at 300ºC with a DC voltage stress of 40 V, presumably indicating a field-sensitive dielectric relaxation effect close to the film T_g of 330ºC for FPE.

From the viewpoint of energy storage considerations, RT dielectric breakdown measurements were performed on the polymer films with 3 mm Al electrodes which were already subjected to high temperature LCR measurements. Average measured breakdown strengths based on various 6F-Co-PBO and FDAPE films ranged from 240 to 245 V/μm while it was measured to be 440V/μm under the same experimental conditions for the FPE film. However, optimization of the current solvent–based laboratory scale thin film fabrication process can potentially lead to higher film breakdown strengths for both FDAPE and 6F-Co-PBO films.

6.0   Recommendations

The research conducted in this program revealed the significance of polymer film thermal and thermo-mechanical properties for potential utilization as high temperature dielectrics in AF wide-temperature power electronics applications. Thermally and mechanically robust thin dielectric films are required for long-term electro-mechanical stability of AF power conditioning capacitors. The comparative dielectric stability studies, as a function of repeated thermal cycling in the RT-350ºC range for 6F-Co-PBO, FDAPE and FPE films, indicated that at least in terms of TCC, no discernible, qualitative differences could be found between the films. It was somewhat surprising that the wide-temperature dielectric stability of the FPE film in the RT-350ºC range was comparable to that of 6F-Co-PBO and FDAPE though its T_g (330ºC) was much lower than those of both 6F-Co-PBO and FDAPE (375ºC and 450ºC respectively). Among the three films, FDAPE film exhibited a much lower temperature-dependent DF and a higher insulation resistance in the RT-350ºC range than both 6F-Co-PBO and FPE films and could be a potential candidate with long-term stability for utilization in wide-temperature power conditioning capacitor applications.

While profound distinctions between the polymer films in short-term dielectric stability did not emerge from these studies, long-term dielectric stability at the highest temperature of operation (350ºC) is an aspect that needs to be investigated in the future. Isothermal LCR measurements of the metalized polymer films can be conducted over several days at 350ºC to examine the issue of thermal endurance of the capacitor. Dimensional changes at temperatures close to or exceeding polymer T_g could be of great significance in determining long-term dielectric performance. The current automated LCR program in the RZPE capacitor laboratory can certainly be used to conduct these extended dielectric experiments.

Isothermal aging (ITA) experiments over 500 or 1000 hours duration need to be performed in both inert atmosphere as well as in air at 300ºC and 350ºC. While the inert atmosphere aging experiments will point to the potential of the dielectrics for reliable operation in hermetically-sealed capacitors, the corresponding ITA experiments in air will examine the potential of the polymer films for long-term capacitor operation in an ambient environment at high temperatures.

Besides thermal endurance, the influence of voltage stress on wide-temperature dielectric stability should also be investigated, by biasing the sample under AC or DC conditions during thermal cycling. Voltage endurance tests targeted to distinguish between various high temperature films for power system conditioning capacitor applications should be performed. Preliminary variable temperature LCR experiments with the application of DC voltage stress up to 40 V revealed that profound increase in DF at high temperatures could result in the case of some films, presumably indicating field-sensitive dielectric relaxation effects, especially close to the T_g of the film. This set of wide-temperature LCR experiments has to be expanded with the application of voltage as high as 200V or more, based on the requirements for a DoD-specific technology.

Optimization of the fabrication of solution-cast thin films on the laboratory-scale needs to be addressed in order to minimize morphological defects. This can potentially lead to the production of thin films with higher breakdown strengths required for high energy density capacitors. The

potential for roll-to-roll processing/manufacturing of FDAPE and 6F-Co-PBO films needs to be explored as well in an extended program.

One of the thermal management issues concerning polymer-film based capacitors for high temperature operation is the CTE mismatch between the dielectric and the electrode. This should be addressed in candidate high temperature polymer films by the incorporation of suitable nano-particles such as α-Al_2O_3 or nanodiamond which are known to exhibit a low CTE and a high thermal conductivity. The suitably nano-dispersed phase in the dielectric matrix can also enhance the dielectric constant of the film to provide higher energy density.

7.0　　References

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Appendix

Presentation Abstracts, Conference Proceedings and Publications

1. N. Venkat, T. D. Dang, Z. Bai, V. K. McNier, J. N. DeCerbo, B-H. Tsao, and J. T. Stricker, "High Temperature Polymer Film Dielectrics for Aerospace Power Conditioning Capacitor Applications", SAMPADA-2008 (2nd International Symposium on Advanced Materials and Polymers for Aerospace and Defense Applications), December 8-12, Pune, India (*Materials Science & Engineering: Part B*, **2010, in print**).

Abstract:

Polymer dielectrics are the preferred materials of choice for capacitive energy-storage applications because of their potential for high dielectric breakdown strengths, low dissipation factors and good dielectric stability over a wide range of frequencies and temperatures, despite having inherently lower dielectric constants relative to ceramic dielectrics. They are also amenable to large area processing into films at a relatively lower cost. Air Force currently has a strong need for the development of compact capacitors which are thermally robust for operation in a variety of aerospace power conditioning applications. While such applications typically use polycarbonate (PC) dielectric films in wound capacitors for operation from -55ºC to 125ºC, future power electronic systems would require the use of polymer dielectrics that can reliably operate up to elevated temperatures in the range of 250-350°C. The focus of this research is the generation and dielectric evaluation of metallized, thin free-standing films derived from high temperature polymer structures such as fluorinated polybenzoxazoles, post-functionalized fluorinated polyimides and fluorenyl polyesters incorporating diamond-like hydrocarbon units. The discussion is centered mainly on variable temperature dielectric measurements of film capacitance and dissipation factor and the effects of thermal cycling, up to a maximum temperature of 350ºC, on film dielectric performance. Initial studies clearly point to the dielectric stability of these films for high temperature power conditioning applications, as indicated by their relatively low temperature coefficient of capacitance (TCC) (~ 2 %) in film capacitance over the entire range of temperatures. Some of the films were also found to exhibit good dielectric breakdown strengths (up to 460V/µm) and a film dissipation factor of the order of < 0.003 (0.3 %) at the frequency of interest (10 kHz) for the intended applications. The measured relative dielectric permittivities of these high temperature polymer films were in the range of 2.9-3.5.

2. N. Venkat, V. K. McNier, B-H. Tsao, T. D. Dang, J. N. DeCerbo and J. T. Stricker, "High Performance Polymer Film Dielectrics for Air Force Wide temperature Power Electronics Applications", *CARTS USA* (March 30-April 2, Jacksonville, Florida), pp. 65-81, **2009**.

Abstract:

Air Force currently has a strong need for the development of compact capacitors which are mechanically robust and thermally stable for operation in a variety of aerospace power conditioning applications. These applications demand better reliability and flexibility in the power system design as well as decreased thermal load for electronic system cooling. While power conditioning capacitors typically use polycarbonate (PC) dielectric films in wound capacitors for operation from -55ºC to 125ºC, future power electronic systems would require the use of polymer dielectrics that can reliably operate at elevated temperatures up to or even exceeding 350ºC.

The focus of this research is the generation and dielectric evaluation, up to 350ºC, of metallized free-standing thin films derived from high temperature polymer systems such as fluorinated polybenzoxazoles (6F-PBO) and fluorenyl polyesters incorporating diamond-like hydrocarbon units (FDAPE). The discussion will be centered mainly on variable temperature dielectric measurements of film capacitance, dissipation factor and insulation resistance and the effects of thermal cycling on film dielectric performance. Initial studies clearly point to the dielectric stability of these films for high temperature power conditioning applications, as indicated by relatively minor variations (~ 2 %)

in measured film capacitance over the entire range of temperatures studied. Comparison will also be made with the reported variable temperature dielectric properties of the state-of-the-art high temperature FPE films.

3. "Designing high performance polymer dielectrics for wide-temperature power electronics applications", **N. Venkatasubramanian**, narayanan.venkat@wpafb.af.mil[1], Zongwu Bai, zongwu.bai@wpafb.af.mil[1], Jeffery T. Stricker, jeffery.stricker2@wpafb.af.mil[2], and Thuy D. Dang, thuy.dang@wpafb.af.mil[3], presented at the Polymeric Materials Science and Engineering (PMSE) Division, American Chemical Society, March 22-26, **2009,** Salt Lake City, Utah (*Polymeric Materials: Science and Engineering* 100, 623-24, **2009**).

Abstract:

The primary focus of the reported dielectric film research is the design and development of high performance polymer dielectrics which are mechanically robust and thermally stable for use in wide-temperature aerospace power conditioning capacitor applications. While power conditioning applications typically use polycarbonate (PC) dielectric films in wound capacitors for operation from -55°C to 125°C, current challenges facing aerospace power electronic applications demand the implementation of a new generation of dielectric materials in energy-storage devices that can operate at elevated temperatures exceeding 350°C. As part of the capacitor research program toward meeting the requirements of dielectric stability and reliability at high temperatures, we report herein the film fabrication and variable temperature dielectric evaluation of some high performance polymers synthesized in our laboratories. The candidate high temperature polymers are based on a fluorinated polybenzoxazole polymer, as well as a fluorinated polyimide and a fluorenyl polyester, both modified with a diamond-like hydrocarbon unit. Initial studies clearly point to the dielectric stability of these films for high temperature power conditioning applications, as indicated by relatively minor variations (~ 2 %) in film capacitance over the entire range of temperatures studied. Film dissipation factors measured at 10 kHz frequency did not show significant variations as a function of thermal cycling.

4. N. Venkat, V. K. McNier, Z. Bai, M. D. Houtz, T. D. Dang, J. N. DeCerbo and J. T. Stricker, "Thermally Robust Polymer Dielectric systems for Air Force Wide-Temperature Power Electronics Applications", Presented at the IMAPS *International Conference, High temperature Electronics Network (HiTEN* **2009**), St. Catherine's College, Oxford, UK, September 13-16, **2009**, Proceedings CD-ROM, pp. 17-23.

Abstract:

Thermally stable, mechanically robust, compact capacitors are the technology driver for high performance power systems. The proximity of power electronics to heat sources demands that the thermal load for electronic system cooling be reduced or eliminated in the new generation aircraft power systems. While aerospace power conditioning capacitors typically use polycarbonate (PC) films in wound capacitors for operation in the -55°C to 125°C range, there is a current need for high temperature polymer film dielectrics with dielectric stability up to 350°C. As part of our program toward meeting the objective of dielectric stability and reliability in capacitor devices at temperatures as high as 350°C, we designed and evaluated high strength polymer films with high glass transition temperatures (375-450°C) as well as high thermal stabilities (470-520°C). Variable temperature dielectric properties of metalized thin films in the RT-350°C range are reported for high temperature polymer systems such as fluorinated polybenzoxazoles (6F-PBO) and a fluorenyl polyester incorporating a diamond-like hydrocarbon unit, known as FDAPE. A comparative dielectric evaluation of the state-of-the-art fluorenyl polyester film FPE, with a glass transition temperature of 330°C, has also been performed. The focus of the study is on wide temperature dielectric measurements of film capacitance, and dissipation factor as well as insulation resistance and the effects of thermal cycling on polymer dielectric stability. Possible correlations between the thermo-mechanical properties of the polymer films and their high temperature dielectric properties are examined, from the viewpoint of their electro-mechanical stability for long- term operation in wide-temperature power electronics applications.

List of Acronyms, Abbreviations, and Symbols

Acronym, Abbreviation, or Symbol	Description
T_g	Glass Transition Temperature
T_d	Degradation temperature
BOPP	Biaxially Oriented Polypropylene
6F-Co-PBO	Fluorinated polybenzoxazole copolymer
FDAPE	Flourenyl Diamantyl Polyester
PI-ADE	Polyimide with adamantyl ester
FPE	Fluorenyl Polyester
LCR	Inductance Capacitance Resistance
DF	Dissipation Factor
ESR	Equivalent Series Resistance
IR	Insulation Resistance
I-V	Current-Voltage
BDV	Breakdown Voltage
TCC	Temperature Coefficient of Capacitance
μm	micrometer
pF	pico-Farad
nF	nano-farad
kHz	Kilo-Hertz
MHz	Mega-Hertz
kV	Kilo-Volt
k	Dielectric Constant
ω	Frequency
μA	micro-Ampere
R_p	Parallel Resistance
RT	Room Temperature
Al	Aluminum
PC	Polycarbonate
PEN	Polyethylene naphthalate)
PPS	Poly(p-phenylenesulfide)
PI	Kapton Polyimide
PTFE	Poly(tetrafluoroethylene)
PPQ	Poly(phenylquinoxaline)
PI-OH	Hydroxy polyimide
THF	Tetrahydrofuran
MSA	Methanesulfonic acid
DMF	N,N-Dimethylformamide
NMP	N-Methylpyrrolidone
DMAc	N, N-Dimethylacetamide
6FDA	4,4'-hexafluoroisopropylidene diphthalic anhydride
TEA	Triethylamine

Acronym, Abbreviation, or Symbol	Description
PPA	Polyphosphoric Acid
TGA	Thermo-Gravimetric Analysis
ITA	Isothermal Aging
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
TMA	Thermo-Mechanical Analysis
Tan δ	Loss Tangent
CTE	Coefficient of Thermal Expansion
E	Tensile Modulus
σ	Tensile Strength
ε	Elongation-at-break
GPa	Giga-Pascals
MPa	Mega-Pascals
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
RU	Ramp Up
RD	Ramp Down
RU2	Ramp Up (second heating cycle)
RD2	Ramp Down (second cooling cycle)
DoD	Department of Defense